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# HEATS OF FORMATION OF METALLIC BORIDES BY FLUORINE BOMB CALORIMETRY

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# FOREWORD

This report was prepared by the National Bureau of Standards under USAF Delivery Order Nr. 33(616)61-09) and Amendments Nr. 1(61-2018), Nr. 2(62-1635) and Nr. 3. The work was initiated under Project Nr. 1(1-3048), Task Nr. 3048-30193 EFFORT, and later changed to Project Nr. (62-6199), Task Nr. 3048-30482 EFFORT. Technical supervision was provided by H. A. Bartick, L. C. Dickey, P. Pitts, and A. E. Zengel of the Research and Technology Division.

This report (NBS Report No. 8153) covers work performed in the period 1 October 1961 to 30 September 1963 under NBS Project 0302-11-03428.

A major task of critical importance to the validity of the studies described here was the procurement of suitable samples of materials to be studied. These were obtained by a cost-sharing arrangement with the Carborundum Company, who cooperated wholeheartedly in the effort to prepare materials of as high a purity as possible in the light of current technology. Dr. V. I. Matkovich of the Carborundum Company devised procedures for synthesis and characterization of the several aluminum, titanium and zirconium borides described in this report, and prepared them, with the exception of those purported to be $ZrB_{28}$, which were obtained from another source.

The purposesof this work were to provide a review of existing thermodynamic data on the metallic borides, and, by new experimental measurements, to augment the existing data on heats of formation of this class of compounds. The data are of immediate application to the combustion of slurries in which solid borides are mixed with a liquid fuel to obtain desirable combustion properties. In addition, the heats of formation of borides are of intrinsic scientific interest, as they are a class of compounds difficult to prepare and, so far, the subject of only a limited amount of valid thermodynamic study.

The authors wish to thank the following personnel for various types of technical assistance: C. F. Coyle, Jr., calculation of data; R. Paulson and J. Maienthal, wet chemical analysis; E. Hughes, mass spectrometric analysis; E. Hubbard, spectrochemical analysis; W. H. Gallagher, density determination; and H. Swanson, crystallographic analysis.

## ABSTRACT

For reactions (1) and (2), the values of $\Delta H^{\circ}_{298}$ were found

$$AlB_{2.215}(s) + \frac{9.645}{2} F_2(g) = AlF_3(s) + 2.215\ BF_3(g) \qquad (1)$$

$$\alpha\text{-}AlB_{11.96}(s) + \frac{38.87}{2} F_2(g) = AlF_3(s) + 11.96\ BF_3(g) \qquad (2)$$

The heats of formation of $AlB_2$ and $AlB_{12}$ were calculated, respectively, to be -923.5 and -3546.2 kcal mole$^{-1}$. The heats of formation, $\Delta H^{\circ}_{f298}$, were calculated for $AlB_{2.215}$ and $\alpha$-$AlB_{11.96}$ to be -34.7 and -42.0 kcal mole$^{-1}$ respectively. Uncertainties of the heats of formation, estimated as the standard deviations of the means, are 2.1 and 1.8 kcal mole, respectively.

The samples were completely analyzed and carefully characterized. Some combustion measurements on impure zirconium borides are reported. A review with 85 references is given of the available thermodynamic data on borides.


This technical documentary report has been reviewed and is approved.

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## 1.1. Introduction

Since the early studies of Moissan [1,2,3] during the 1890's, relatively little work has been done in the field of metallic borides. A renewed interest has been kindled toward investigating refractory compounds for new applications such as space technology, aircraft propulsion systems and the field of semiconductors. It is clear from the researches that have been made that the lack of data on borides can be blamed to a large degree upon the difficulties encountered in preparing and characterizing single phase materials having a definite stoichiometry.

We have undertaken to collect the available thermodynamic data on metallic borides from 1950 up to the present. The presentation of thermodynamic data on metallic borides will be made in three sections. First, a discussion will be made of publications which are of a review nature, or describe comprehensive experimental studies in which thermodynamic properties are reported for many borides. Secondly, thermodynamic data are presented for individual borides. The thermodynamic property under study is reported here along with a brief discussion of the technique used, reactions investigated, temperature interval examined and data calculated. Lastly, a section is given which sums up the collected information with respect to the validity of its comments, criticism of methods, techniques and calculations, and the status of the thermodynamic data compiled.

## 1.2. General Review Publications and Experimental Studies

Schick, Anthrop, Dreikorn, Hanst and Panish [4,5,6] give a critical evaluation of the thermodynamic data for numerous refractory compounds, among which are the diborides of titanium, zirconium, hafnium and niobium. Thermodynamic properties are listed at 0°K, 298.15 °K and at 100° intervals from 300° to 6000 °K for the elements and compounds. The properties listed include: heat capacity, entropy, free energy function, heat content, heat of formation, free energy of formation and log Kp.

Samsonov and Markovskii [7] published an account of the preparation, properties and applications of metallic borides. The book "Boron, Its Compounds and Alloys" by Samsonov, Markovskii, Zhigach, and Valyashko [8] gives a comprehensive survey on boron and metallic borides. The latter two publications give the reader some insight into the effort and progress in the study of refractory borides in the Soviet Union.

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A review paper by Aronsson [9] gives a comprehensive discussion of the available information on the properties, crystallography, general physical properties and phase equilibria of the borides. Particular attention is called by Aronsson to the need for research in the preparation of pure borides with complete chemical analysis. Data of this type would help explain differences among various results and would show the influence of small impurities on the behavior of metal-boron systems. Another paper by Aronsson [10] reviews recent studies on the borides and silicides of the transition elements with particular emphasis on their crystal chemistry.

Schwartzkopf and Kieffer [11] discuss preparation, properties, and phase relationships in their book "Refractory Hard Metals, Borides, Carbides, Nitrides, Silicides". A book by Hansen and Anderko [12] gives phase diagrams and phase relationships of borides among many other compounds, while Pearson [13] gives lattice constants and structural data. Samsonov [14] reports on the chemistry of rare earth metal borides and Markovskii and Kondrashev [15] discuss borides of the first and second groups of the periodic table. Gmelin [16] contains brief accounts of metal-boron systems in the appropriate volumes.

Brewer and Haraldsen [17] studied the equilibria involved in reactions between nitrogen gas and metal borides, and graphite and metal borides from which they obtained information on the relative stabilities of the metal boride phases. They estimated heats of formation on the basis of the stability of a boride phase in the presence of nitrogen gas or graphite at high temperatures. Estimates were also based on the reducibility of a boride phase by other metals.

Mezaki, Tilleux, Barnes and Margrave [18] determined enthalpy as a function of temperature and calculated heat capacity, entropy and enthalpy for fifteen refractory borides: BN cubic, BN hexagonal, $TiB_2$, $ZrB_2$, $HfB_2$, $NbB_2$, TaB, $TaB_2$, CrB, $CrB_2$, $Mo_2B$, $MoB_2$, $W_2B$, WB, and $W_2B_5$. A copper-block "drop" calorimeter was used over the temperature range 400° to 1200 °K.

## 1.3. Data on Individual Metallic Borides

### Aluminum Diboride, $AlB_2$

For calculations of the performance of rocket propellants, Van Arkel [19] assigned a heat of formation of -80 kcal $mole^{-1}$ to aluminum diboride, but gave no source for his value. The usefulness of this value is questionable because of the lack of information about the source.

Aluminum Dodecaboride, $AlB_{12}$

The heat of vaporization of $AlB_{12}$ was determined by Bolgar, Verkhoglyadova and Samsonov [20] using the Langmuir technique. Of the refractory compounds studied by these authors, all were reported to vaporize to a molecular species with the exception of $AlB_{12}$ which dissociated yielding aluminum as one of the products. From the measurements made, the heat of vaporization was calculated to be 45.7 kcal $mole^{-1}$. Calculations were made using the second-law treatment.

Boron Carbide, $B_4C$

Samsonov [23] employed a value for the heat of formation of boron carbide equal to +66.0 kcal $mole^{-1}$ in his study of the reduction of titania by carbon. For this value he refers to a paper by Markovskii, Orshanskii and Prinishnikov [24], who in turn refer to a paper by Tikhonov [25]. Because of its uncommon distribution, or possible renaming, we have not been able to obtain a copy of Tikhonov's publication.

In a review on the physical and chemical properties of carbides, Gaev [26] reports a heat of formation value of +48.12 kcal $mole^{-1}$ for $B_4C$. The source for this heat value is given in another publication by Gaev [27] where it is called "data of the author".

The two values for the heat of formation of boron carbide found in the Russian literature, +66.0 and +48.12 kcal $mole^{-1}$ are considered unreliable because of the obscurity of the source and lack of description of methods used in experiments and calculations. It can be shown that Samsonov [8] in a later publication had used -13.8 kcal $mole^{-1}$ for the heat of formation of boron carbide in preference to the earlier Russian work.

Smith, Dworkin and Van Artsdalen [28] appear to have the only reliable data on boron carbide leading to the calculation of the heat of formation. Using bomb calorimetric techniques, boron carbide was burned in oxygen and the heat of combustion determined. With the aid of this value, and the known heats of formation for boric oxide and carbon dioxide, they calculated the heat of formation of boron carbide to be -13.8 kcal $mole^{-1}$. The same combustion data lead to the value -12.2 kcal $mole^{-1}$ when a more recent value for the heat of formation of boric oxide [29] is used.

The high temperature heat content of boron carbide, $B_4C$, was measured by King [21] between 400° and 1700 °K. The specific heat of $B_4C_3$ was measured by Maksimenko and Polubelova [22] over the temperature range 200° to 1000 °C.

Boron Nitride, BN

Boron nitride exists in two crystalline modifications, a cubic and a hexagonal form. In reporting thermodynamic data on boron nitride in which the crystalline form is not stated, we assume the substance being described is hexagonal BN.

The heat of combustion of hexagonal boron nitride was determined by Dworkin, Sasmor and Van Artsdalen [30] and found to be -90.1 ±0.5 kcal mole$^{-1}$. Using -301.75 kcal mole$^{-1}$ for the heat of formation of amorphous boric oxide, they calculated the heat of formation of hexagonal boron nitride to be -60.7 ±0.7 kcal mole$^{-1}$. Gal'chenko, Kornilov and Skuratov [31] determined the heat of formation of hexagonal boron nitride by direct combination in a bomb calorimeter containing an electric furnace. They calculated the heat of formation of hexagonal boron nitride to be -60.8 ±0.3 kcal mole$^{-1}$. Wise [32] determined the heat of combustion of hexagonal boron nitride in fluorine and calculated the heat of formation of BN to be -59.51 ±0.72 kcal mole$^{-1}$. He used a two-chamber combustion bomb to burn a pellet of boron nitride in 2600 mm. of fluorine. Gross [33] determined the heat of formation of boron nitride by combustion in fluorine and calculated a value of -60.52 ±0.41 kcal mole$^{-1}$. Hildenbrand and Hall [34] measured the dissociation pressure of crystalline boron nitride by the torsion-effusion method over the temperature range 1850° to 2160 °K. Their calculation of the heat of formation of boron nitride resulted in the value -59.8 ±0.6 kcal mole$^{-1}$. Dreger, Dadape and Margrave [35] measured free-evaporative rates on solid boron nitride using a microbalance built inside a vacuum system. Calculations by these authors led to the conclusion that $\Delta H^{\circ}_{f298^{\circ}}$ for boron nitride was $\leq$ -60 ±2 kcal mole$^{-1}$. Stull [36] from the bomb combustion of boron and boron nitride in $NF_3$ has obtained -61 ±2 kcal mole$^{-1}$ for $\Delta H^{\circ}_{f298^{\circ}K}$ (BN). Haldeman [37] using oxygen bomb calorimetric techniques to burn boron nitride obtained -61 ±2 kcal mole$^{-1}$ for $\Delta H^{\circ}_{f298^{\circ}}$ (BN).

From these recent measurements, summarized in Table 1.30, one can infer that the heat of formation of boron nitride is known with an uncertainty no more than one kcal mole$^{-1}$, despite other less concordant data mentioned below.

Apin, Lebedev and Nefedova [38] investigated the interaction of nitrogen with metals during explosion. From the heat of the following reaction:

$$PbN_6(s) + B(s) \rightarrow BN(s) + Pb(s) + \frac{5}{2}N_2(g) \quad \Delta H = -134.42 \text{ kcal mole}^{-1}$$

and the heat of formation of lead oxide, -107.76 kcal mole$^{-1}$, they calculated the heat of formation of boron nitride to be -29.7 kcal mole$^{-1}$.

The heat capacity of boron nitride was determined by Stull and Prophet [39] using an arc-image furnace over the temperature range 1300° to 2300 °K. Mezaki et al [16] determined the heat capacity, entropy and enthalpy for hexagonal and cubic boron nitride over the temperature range 298° to 1200 °K. Fesenko [40] studied the dissociation of boron nitride over the temperature range 2500° to 3000 °K. Above 2500 °K, gaseous B, $N_2$, and BN are formed upon sublimation of solid boron nitride. The partial pressure of BN is two orders of magnitude less than that of nitrogen in the temperature range studied. The calculated heat of dissociation and sublimation between 2500° and 3000 °K were found to be -163 kcal $mole^{-1}$, and -160 kcal $mole^{-1}$, respectively.

TABLE 1.30

HEAT OF FORMATION OF BORON NITRIDE

| Heat of Formation $\Delta H^{\circ}_{f298}$ kcal $mole^{-1}$ | Investigators | Reference |
|---|---|---|
| -60.3 | Dworkin, Sasmor, and Van Artsdalen | [30] |
| -60.7 | Gal'chenko, Kornilov and Skuratov | [31] |
| -59.51 | Wise | [32] |
| -60.52 | Gross | [33] |
| -59.8 | Hildenbrand and Hall | [34] |
| -60 | Dreger, Dadape, and Margrave | [35] |
| -61 | Stull | [36] |
| -61 | Haldeman | [37] |

Boron Phosphides, BP and $B_{13}P_2$

An investigation of the temperature dependence of the following equilibrium between 1190° and 1543 °K was made by Stone and his co-workers [41]:

$$BCl_3(g) + \frac{3}{2} H_2(g) + \frac{1}{4} P_4(g) \rightleftarrows BP(s) + 3HCl(g)$$

A least squares calculation of the relationship between the equilibrium constant and temperature resulted in the following equation:

$$\log K_1 = 1.740 - \frac{2110}{T}$$

With this equation and the aid of other thermal data, they calculated the heat of formation of BP(s) to be -19.9 kcal $mole^{-1}$.

Further decomposition of BP(s) was viewed as proceeding by the following reaction:

$$BP(s) \rightleftarrows \frac{1}{6} B_6P(s) + \frac{5}{12} P_2(g)$$

However, Myers [42] points out that because of the findings of Matkovich [43] the dissociation reaction is more likely to be:

$$\frac{26}{11} BP(s) \rightleftarrows \frac{2}{11} B_{13}P_2(s) + P_2(g)$$

X-ray and chemical analysis in conjunction with density determinations of the decomposition product of BP(s) suggest the stiochiometry to be $B_{13}P_2$ and not $B_6P$.

A least squares calculation of the relationship between equilibrium constant and temperature gave the following equation:

$$\text{Log } K_2 = 3.134 - \frac{5900}{T}$$

Using this equation and other thermal data, they calculated the heat of formation of $B_{13}P_2$ to be -31 kcal $mole^{-1}$.

Cerium Hexaboride, $CeB_6$

Brewer and Haraldsen [17] heated cerium metal with boron and boron nitride in a nitrogen atmosphere at 2280 °K, finding no cerium borides in the reaction products. They inferred that cerium borides are less stable than cerium nitrides at 2280 °K. Further experiments showed that cerium hexaboride is stable in the presence of graphite at 2050 °K, while cerium tetraboride is not. Reactions of cerium and boron mixed with molybdenum, tungsten, niobium or tantalum showed no formation of cerium borides. They estimated the heat of formation of cerium tetraboride to be > -84 kcal $mole^{-1}$.

Samsonov and Grodstein [44] measured the vapor pressure of the following reaction using the vacuum-thermal technique of Samsonov and Meerson [45]:

$$CeO_3(s) + 3B_4C(s) \rightleftarrows 2CeB_6(s) + 3CO(g)$$

They determined the equilibrium constant from the measured pressure, and with the aid of other thermodynamic data which is not mentioned in the publication, calculated the heat of formation of cerium hexaboride to be -81 ±16 kcal $mole^{-1}$.

Chromium Borides, CrB and $CrB_2$

The reaction of a mixture of chromium, boron and BN with nitrogen was studied by Brewer and Haraldsen [17]. They found that chromium borides are stable at temperatures above 1820 °K and upon cooling are converted to chromium of $Cr_2N$. They estimated the heat of formation for $\frac{1}{x}\ CrB_x$ for $(x < 2)$ and $\frac{1}{2}\ CrB_2$ to be $< -15$ kcal mole$^{-1}$. Samsonov and Kotelnikov [47] calculated the heat of formation of chromium diboride from vapor pressure measurements similar to those described in reference [23]. The reaction studied was not given, but was probably of the type:

$$Cr_2O_3(s) + B_4C(s) \rightleftarrows 2CrB_2(s) + 3CO(g)$$

From the pressure data and other thermodynamic data, neither of which were given in the paper, they estimated the heat of formation of $CrB_2$ to be -19 kcal mole$^{-1}$. Samsonov [47] also calculated the heat of formation of chromium diboride using an empirical relation of Kubaschewsky and Evans [48] between the heat of formation of a compound and the change in molar volume resulting on forming the compound from its elements. He found $\Delta H^\circ_{f298^\circ}$ to be -47 kcal mole$^{-1}$.

Bolgar, Verkhoglyadova and Samsonov [20] determined the vapor pressure of chromium diboride using the Langmuir technique over the temperature range 1100° to 2000 °C. The authors assumed the volatile species to be molecular $CrB_2$ and using the second-law treatment calculated the heat of vaporization in the temperature range studied to be 41.2 kcal mole$^{-1}$.

Krestovnikov and Vendrikh [46] measured the heat capacity of chromium diboride in the temperature range 300° to 1000 °K. Over this temperature range, the value of the heat capacity of $CrB_2$ changed from 12.36 cal deg$^{-1}$mole$^{-1}$ to 22.99 cal deg$^{-1}$ mole$^{-1}$. Although agreement between experiments was satisfactory between 300° and 800 °K, the authors expressed a need for further work from 800° to 1000 °K.

Mezaki et al [18] have made enthalpy measurements on CrB and $CrB_2$ and calculated heat capacity, entropy and enthalpy data over the temperature range 298° to 1200 °K.

Hafnium Diboride, $HfB_2$

The partial pressure of carbon monoxide in the following equilibrium was measured by Paderno, Serebryakova, and Samsonov [50]:

$$2HfO_2(s) + B_4C(s) + 3C(s) \rightleftarrows 2HfB_2(s) + 4CO(g)$$

They reported that hafnium diboride is formed over the temperature range 1300° to 1600 °C, and calculated the heat of formation of $HfB_2$ to be -74.2 kcal mole$^{-1}$. No mention is made in the abstract of other thermodynamic data needed for the calculation.

Using the Knudsen effusion technique, Krupka [49] studied the vaporization behavior of hafnium diboride over the temperature range 2175° to 2500 °K. His analysis of the data showed that $HfB_2$ vaporizes predominantly as follows:

$$HfB_{1.955}(s) \rightleftarrows Hf(g) + 1.955\ B(g)$$

Krupka calculated the standard heat of vaporization of $HfB_2$ to the gaseous atoms, $\Delta H^\circ_0$, to be 477.8 ±5.5 kcal $mole^{-1}$.

From high temperature enthalpy measurements, Mezaki et al [18] calculated the heat capacity, entropy, and enthalpy of hafnium diboride over the temperature range 298° to 1200 °K. A copper-block "drop" calorimeter was used to obtain the enthalpy data.

Lanthanum Hexaboride, $LaB_6$

By heating cylindrical briquettes of $La_2O_3$ and $B_4C$ in a vacuum furnace, Samsonov, Paderno and Kreingold [51] showed than lanthanum hexaboride begins to form at 1200° to 1300 °C and is complete in one hour at 1500° to 1600 °C.

$$La_2O_3(s) + 3B_4C(s) \rightleftarrows 2LaB_6(s) + 3CO(g)$$

Completeness of the reaction was determined by elemental and X-ray analysis of the sample after an experiment. Using the assumption that at the start of the reaction the system was under approximately equilibrium conditions, they calculated the heat of reaction and heat of formation. For $LaB_6$ they give $\Delta H^\circ_{f298} = -112.3 \pm 6.5$ kcal $mole^{-1}$. The calculations were based upon the data of Kubaschewsky and Evans [48] for $La_2O_3$, $B_4C$ and CO. Pressure or temperature data observed for the reactions were not mentioned, making a re-calculation impossible.

These same authors measured the heat capacity of lanthanum hexaboride over the temperature range 245° to 1210 °C. Description of the calorimeter system is very brief and does not give much basis for estimating the accuracy of the measurements. The variation of the heat capacity with temperature is given by the equation:

$$Cp\ (LaB_6)_{\text{cal deg}^{-1}\text{ mole}^{-1}} = 21.73 + 20.4 \times 10^{-3}\ T$$

Magnesium Borides, $MgB_2$ and $MgB_4$

The heat capacity of magnesium diboride and magnesium tetraboride were measured by Swift and White [52] in the temperature range 18° to 305 °K. They tabulated values for the heat capacity, entropy, enthalpy and free energy functions at integral temperatures.

Molybdenum Borides, $Mo_2B$, $Mo_3B_2$, MoB, $MoB_2$ and $Mo_2B_5$

Gilles and Pollock [53] studied the molybdenum-boron system by the Langmuir method and determined the partial pressures of the elements in equilibrium with the solid boride phases. They calculated the heats of formation of the molybdenum borides from the vapor pressure data assuming that both $\Delta Cp$ and $\Delta S$ for the solid reactions were zero. The results of their calculations are listed in Table 1.31.

TABLE 1.31

HEATS OF FORMATION OF MOLYBDENUM BORIDES FROM GILLES AND POLLOCK [53]

| Boride Phase | Heat of Formation, $\Delta H^\circ_{f298}$ kcal mole$^{-1}$ |
|---|---|
| $Mo_2B$ | -25.5 ±6 |
| $Mo_3B_2$ | -41.9 ±10 |
| $MoB_{0.96}$ | -16.1 ±5 |
| $MoB_{1.06}$ | -16.6 ±6 |
| $MoB_{2.14}$ | 19.7 ±8 |
| $MoB_{2.33}$ | -20.0 ±8 |

Niobium Diboride, $NbB_2$

Brewer and Haraldsen [17] found niobium diboride to be stable in the presence of graphite at 2050 °K, and from metal exchange reactions found it to be more stable than cerium borides at 1775 °K. From the reaction:

$$2NbC(s) + B_4C(s) \rightleftarrows 2NbB_2(s) + 3C(s) \quad (2050°K)$$

and the heats of formation of $B_4C$ [28] and NbC [54] they estimated the heat of formation of $NbB_2$ to be $< -37$ kcal mole$^{-1}$.

Samsonov [47] estimated the heat of formation of niobium diboride from an empirical relation by Kubaschewsky and Evans [48] and found it to be -59 kcal mole$^{-1}$. In a study using a correlation between the heat of formation and electronic configuration of various transition metal borides, carbides and nitrides, Samsonov [47] estimated another value for the heat of formation of $NbB_2$, -33.5 kcal mole$^{-1}$.

From preliminary work on an impure sample of niobium diboride, Huber [55] reports a heat of formation of $NbB_2$ of -42 kcal mole$^{-1}$. Westrum and Clay [56] measured the heat capacity of nonstoichiometric $NbB_{1.963}$ in an adiabatic calorimeter and calculated the heat capacity, entropy, enthalpy and free energy function over the temperature range 5° to 350 °K.

Silicon Hexaboride, $SiB_6$

Knarr [57] studied the vapor pressure of silicon hexaboride by the Knudsen effusion method. Use of the second-law method with the vapor pressure data gave Knarr values of 119.02 ±2.6 kcal $mole^{-1}$ and 36.53 ±1.29 cal $deg^{-1}$ $mole^{-1}$ for the enthalpy and entropy of vaporization of Si from $SiB_6$ to form a boron residue. For the same process, the third-law method gave him 113.4 kcal $mole^{-1}$ and 33.85 cal $deg^{-1}$ $mole^{-1}$ for the enthalpy and entropy of vaporization, respectively. Knarr estimated the enthalpy and entropy of formation of $SiB_6$ to be -7.00 kcal $mole^{-1}$ and 1.33 cal $deg^{-1}$ $mole^{-1}$.

Strontium Hexaboride, $SrB_6$

Samsonov, Serebryakova and Bolgar [58] determined the heat of formation of strontium hexaboride by measuring the partial pressure of carbon monoxide in the following equilibrium at 1800 °C at which temperature it was determined that boride formation predominates.

$$SrO(s) + B_4C(s) + 2B(s) \rightleftarrows SrB_6(s) + CO(g)$$

In conjunction with other thermodynamic data, which are not given in the paper, they calculated the heat of formation of strontium hexaboride to be approximately -50.4 kcal $mole^{-1}$.

Bolgar, Verkhoglyadova, and Samsonov [20] determined the heat of vaporization of strontium hexaboride using the Langmuir method over the temperature range 1400° to 2100 °C. Assuming the vapor to be monomeric $SrB_6$ and using the second-law method they calculated the heat of vaporization to be 97.9 kcal $mole^{-1}$. The authors gave the following pressure-temperature equation for strontium hexaboride over the temperature range studied:

$$\text{Log } P_{mm} = 6.36 - \frac{21428}{T}$$

Tantalum Borides, $Ta_2B$, $Ta_3B_2$, TaB, and $TaB_2$

Brewer and Haraldsen [17] found tantalum diboride to be stable in the presence of graphite at 2050 °K. They also found that tantalum metal reduces molybdenum and tungsten borides. From its equilibrium with gaseous boron and solid tantalum, they estimated the heat of formation of tantalum diboride to be $< -45$ kcal $mole^{-1}$.

Leitnaker, Bowman and Gilles [59] found tantalum metal on the surfaces of samples of various tantalum borides after they had been subjected to high temperature vaporization. In this way they demonstrated that gaseous boron is lost preferentially from all tantalum borides at high temperatures by a process of which the following equation is typical.

$$Ta_{2.4}B(s) \rightleftarrows 2.4\ Ta(s) + B(g)$$

Assuming that $\Delta S$ for the reaction is zero and using selected values for the vapor pressure of tantalum metal at 2000 °K, the heat of sublimation of boron and free energy functions for $Ta_2B$, Ta and B, they calculated the heat of formation of $Ta_{2.4}B$ to be $> -64.9$ kcal mole$^{-1}$. Observation of equilibria between $Ta_2B$, $Ta_3B_2$, TaB and tantalum metal led them to the conclusion that $\Delta H^\circ_{f298}$ is nearly the same per boron atom for the three borides. The failure of TaB to reduce zironium diboride was taken by Leitnaker et al to show that the following reaction would take place:

$$2TaB_2(s) + Zr(s) \rightarrow 2TaB(s) + ZrB_2(s)$$

Using the value found by Huber, Holley and Head [60] for the heat of formation of $ZrB_2$, -76.7 kcal mole$^{-1}$, and -64.9 for TaB, they showed that $\Delta H^\circ_{f298}$ for $TaB_2$ is more negative than -45 kcal mole$^{-1}$. They placed the following limits on the heats of formation of the tantalum borides:

| Boride Phase | Heat of Formation, $\Delta H^\circ_{f298}$ kcal mole$^{-1}$ |
|---|---|
| $Ta_{2.4}B$, $Ta_{1.6}B$, TaB | -38.4 to -64.9 |
| $1/2TaB_2$ | -22.7 to -51.7 |

Samsonov [47] estimated the heat of formation of tantalum diboride to be -63 kcal mole$^{-1}$ from an empirical equation by Kubaschewsky and Evans [48] relating the heat of formation to the change in molar volume upon formation of a compound from its elements. Another estimate of the heat of formation of $TaB_2$ was obtained from a correlation of heat of formation with electronic configuration of transition metal borides, carbides, and nitrides. Using this approach Samsonov obtained -45 kcal mole$^{-1}$.

Thorium Borides, $ThB_4$ and $ThB_6$

Brewer and Haraldsen [17] found that thorium hexaboride is stable in the presence of graphite at high temperatures, while thorium tetraboride is not. The heats of formation of $ThB_4$ and $ThB_6$ were estimated to be $< -54$ kcal mole$^{-1}$ and $< -66$ kcal mole$^{-1}$, respectively.

Titanium Diboride, $TiB_2$

Brewer and Haraldsen [17] concluded from their experiments that titanium diboride is largely converted to TiN in the presence of nitrogen at 1820 °K, but is quite stable at 2270 °K. Assuming that the equilibrium constant is unity for the following equilibrium at 1820 °K:

$$TiB_2(s) + 3/2\ N_2(g) \rightleftarrows TiN(s) + 2BN(s)$$

and that $\Delta S^\circ$ and $\Delta C_p^\circ$ for the reaction are approximately zero, they estimated a heat of formation of -72 kcal mole$^{-1}$ for titanium diboride. The following generalizations were also made: for $\frac{1}{x}TiB_x$ with $(x < 2)$, $\Delta H^\circ_f$ is $\sim -36$ kcal mole$^{-1}$, and for $Ti_2B_5$ $\Delta H^\circ_f$ is $\sim -105$ kcal mole$^{-1}$.

Using a vacuum-thermal technique, Samsonov [23] determined the partial pressure of carbon monoxide in the system TiO-$B_4C$-C at 1393 °K. He associated the observed pressure with the equilibrium pressure of CO in the following reaction:

$$2TiO(s) + B_4C(s) + C(s) \rightleftarrows 2TiB_2(s) + 2CO(g)$$

From the pressure of CO, and thermodynamic values for TiO, $B_4C$, C, and CO, he calculated the heat of formation of titanium diboride to be 70.04 kcal $mole^{-1}$. The fact that a rate of change of pressure was observed rather than an actual equilibrium suggests that the results were probably only semi-quantitative. The merits of the vacuum-thermal technique used by Samsonov are discussed more fully in Section 1.4. Further complications stem from the use of unreliable auxiliary data in the calculation.

Samsonov [47] gives a value of -73 kcal $mole^{-1}$ for the heat of formation of titanium diboride based on an empirical relation by Kubaschewsky and Evans [48] between the heat of formation of a compound and the change in molar volume upon formation of the compound from its elements.

Williams [61] reinvestigated the following equilibrium previously studied by Brewer and Haraldsen [17]:

$$TiN(s) + 2BN(s) \rightleftarrows TiB_2(s) + 3/2N_2(g)$$

Williams found the equilibrium or transition temperature to be 2150° ±25 °K rather than 1820 °K. He also pointed out that the value for $\Delta F^\circ_{f298}$ of BN used by Brewer and Haraldsen was in error. Using different data, Williams modified Brewer and Haraldsen's estimate for $\Delta H^\circ_{f298}$ for titanium diboride to ~-84 kcal $mole^{-1}$. Williams also critically discusses the previous work on the heat of formation of titanium diboride in comparison with his own, and cites probable errors in the earlier work [17,23,47].

Lowell and Williams [62] measured the heat of formation of titanium diboride by direct combination of the elements in a high temperature calorimeter.

$$Ti(s) + 2B(s) \rightarrow TiB_2(s)$$

The value they determined for $\Delta H^\circ_{f298}$ was -50 ±5 kcal $mole^{-1}$.

Schissel and Trulson [63] used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system. They determined the pressures of Ti(g) and B(g) over several condensed phases and from their data calculated 430 kcal $mole^{-1}$ for the heat of vaporization at 298 °K and -52 kcal $mole^{-1}$ for the heat of formation ($\Delta H^\circ_{f298}$)

of titanium diboride. These authors suggest that in earlier work by Schissel and Williams [64], which led to -32 kcal $mole^{-1}$ for the heat of formation of $TiB_2$, measurement of the Ti(g) pressure was in error. They ascribed the anomalously high Ti(g) pressure to a possible escape of titanium vapor induced by a reaction with tungsten.

Epel'baum and Starostina [65] determined the heats of combustion of boron and of titanium diboride by oxygen bomb calorimetry. They obtained heats of formation of -66.85 ±2.68 kcal $mole^{-1}$ for $TiB_2$, and two values, 287.8 ±2.17 or 289.47 ±3.1 kcal $mole^{-1}$ for $B_2O_3$. The heat of combustion of boron reported by these authors is somewhat different from the presently accepted value ($\Delta H^{\circ}_{f298}$ for $B_2O_3$ = -305.34 ±0.33 kcal $mole^{-1}$ [29,66], suggesting that the combustion of boron was incomplete. The combustion experiments on $TiB_2$ are also subject to uncertainty because of possible incomplete combustion.

Bolgar, Verkhoglyadova, and Samsonov [20] measured the vapor pressure of titanium diboride over the temperature range 1100° to 2000 °C by means of the Langmuir technique. Assuming the vapor to be monomeric $TiB_2(g)$, they calculated a heat of vaporization of 45.7 kcal $mole^{-1}$ from a second-law treatment of the experimental data.

From high temperature heat content measurements, Mezaki et al [18] have calculated the heat capacity, entropy, and heat content of titanium diboride over the temperature range 298° to 1200 °K.

Krestovnikov and Vendrikh [67] calculated the entropy as a function of temperature for titanium, boron, and titanium diboride, and also the entropy of formation of $TiB_2$ from their experimental measurements of the heat capacities of these substances between 298° and 3253 °K. From an analysis of the heat of formation reported for $TiB_2$ by Samsonov [23] and Brewer and Haraldsen [17], they adopted a value of -70.00 kcal $mole^{-1}$.

Walker, Ewing and Miller [68] determined the heat capacity of titanium diboride over the temperature range 30° to 700 °C.

Barriault et al [69] performed an experimental heat capacity study on a 92% pure sample of titanium diboride over the temperature range 1733° to 2417 °K. A rate-of-cooling technique was used by Prophet [70] to determine the heat capacity in the range 1300° to 2150 °K. Another heat capacity study was reported by the Southern Research Institute [71] over the temperature range 533° to 2755 °K.

Tungsten Borides, $W_2B$, WB, $W_2B_5$

Brewer and Haraldsen [17] found that WB and $W_2B_5$ are stable at high temperatures with respect to graphite, while $W_2B$ reacts with graphite to form WC and WB. They found the stabilities of the tungsten borides to be about the same as those of the molybdenum borides. Using the data of Gilles and Pollock [53] on the heats of formation of the molybdenum borides

as a guide, Brewer and Haraldsen estimated heats of formation for the tungsten borides shown in Table 1.32.

TABLE 1.32

HEATS OF FORMATION OF TUNGSTEN BORIDES
FROM BREWER AND HERALDSEN [17]

| Compound | Estimated $\Delta H^{\circ}_{f298}$°K kcal mole$^{-1}$ |
|---|---|
| $W_2B$ | -20 to -28 |
| WB | -12 to -22 |
| $W_2B_5$ | -25 to -45 |

Leitnaker, Bowman and Gilles [59] found that tungsten does not react with zirconium diboride in vacuum between 2075° and 2140 °C. From this they concluded that the partial pressure of boron in equilibrium with $ZrB_2$ is less than that in equilibrium with tungsten and $W_2B$. Using available data on the partial pressure of boron over $ZrB_2$, they estimated the heat of formation of $W_2B$ to be -20 to -26 kcal mole$^{-1}$.

Uranium Borides, $UB_2$ and $UB_4$

Equations for the heat capacities of uranium diboride and uranium tetraboride between room temperature and 2000 °K were estimated by Tripler, Snyder, and Duckworth [72] using a method of Kubaschewsky and Evans [48]. They also estimated standard free energy of formation equations for uranium diboride from room temperature to 1400 °K.

Vanadium Diboride, $VB_2$

Samsonov [47] calculated the heat of formation of vanadium diboride to be -62 kcal mole$^{-1}$ using an empirical equation by Kubaschewsky and Evans [48] relating the heat of formation of a compound to the change in molar volume upon formation of the compound from its elements. From a correlation of the heats of formation of various transition metal borides, carbides and nitrides with their electronic structures, Samsonov estimated the heat of formation $VB_2$, and found $\Delta H_{f298}$, -24 kcal mole$^{-1}$.

Yttrium Hexaboride, $YB_6$

Measurements of the partial pressure of carbon monoxide were made over the temperature range 880° to 1900 °C by Kudinstseva, Polyakova, Samsonov and Tsarev [73] for the reaction:

$$Y_2C_3(s) + 3B_4C(s) \rightleftarrows YB_6(s) + 3CO(g)$$

The authors reported a pressure discontinuity at 970 °C and deduced that the reaction was singular without the formation of lower yttrium oxides. Using the following values: $S°(YB_6) = 10.58$ cal $deg^{-1}$ $mole^{-1}$ and $S°(Y_2O_3) = 10.52$ cal $deg^{-1}$ $mole^{-1}$, they calculated an approximate value for the heat of formation for $YB_6$, $\Delta H°_{f298} = -24$ kcal $mole^{-1}$. The entropy values were calculated from empirical formulas in Kubaschewsky and Evans [48]. Unfortunately, this value cannot be checked because other necessary data, such as the observed pressure at the discontinuity 970 °C are not given. Also lacking are values they used for the heats of formation of $Y_2O_3$, $B_4C$ and CO.

Zirconium Diboride, $ZrB_2$

Brewer amd Haraldsen [17] estimated the heat of formation of zirconium diboride on the basis of studies of high temperature reactions of zirconium and boron with (1) graphite, (2) nitrogen, and (3) boron nitride and nitrogen. Metal exchange reactions showed that zirconium reduces molybdenum and tungsten borides. They calculated heats of formation per gram-atom of boron to be $< -39$ kcal $mole^{-1}$ for ZrB and $\frac{1}{2}ZrB_2$, and $< -10$ kcal $mole^{-1}$ for $\frac{1}{12}ZrB_{12}$. Epel'baum and Starostina [65] burned zirconium diboride in oxygen and calculated the heat of formation of $ZrB_{2.05}$ to be $-75.02 \pm 3.35$ kcal $mole^{-1}$. Since the heat of combustion of boron obtained by these authors is less negative than that suggested by a recently accepted value for the heat of formation of $B_2O_3$ [66], their measurements on $ZrB_{2.05}$ are subject to uncertainties both in the degree of completeness of combustion, and in the values used for auxiliary data. Leitnaker, Bowman and Gilles [60] quote a value for the heat of formation of $ZrB_2$ equal to $-76.7$ kcal $mole^{-1}$ as being the work of Huber, Head and Holley. The latter investigators burned zirconium diboride in an oxygen bomb and measured the heat of combustion. The heat of combustion of $ZrB_2$ in fluorine was measured by Hubbard et al [76]. They calculated $\Delta H°_{f298}$ for $ZrB_2$ to be $-71.5$ kcal $mole^{-1}$. Samsonov [47] reported the heat of formation of zirconium diboride from a determination of the equilibrium pressure of carbon monoxide at elevated temperatures.

$$ZrO_2(s) + B_4C(s) + 3C(s) \rightleftarrows 2ZrB_2(s) + 4CO(g)$$

No data are given for the pressures observed or any thermodynamic data used in the calculation. The value for the heat of formation of $ZrB_2$ given is $-63.1$ kcal $mole^{-1}$. Using an empirical equation given by Kubaschewsky and Evans [48] relating the heat of formation of a compound to the change in molar volume upon formation of the compound from its elements, Samsonov [47] calculated $\Delta H°_{f298}$ for $ZrB_2$, $-65$ kcal $mole^{-1}$. Another estimate was obtained fro a correlation of the heats of formation of varicus transition metal borides, carbides and nitrides with their electronic configuration yielding $\Delta H°_{f298}$, for $ZrB_2$, $-60$ kcal $mole^{-1}$.

Leitnaker, Bowman and Gilles [60] measured the vapor pressure of zirconium over zirconium diboride in the temperature range 2150° to 2475 °K using the Knudsen method for the following reaction:

$$ZrB_{1.906}(s) \rightleftarrows Zr(g) + 1.906\ B(g)$$

They calculated the heat of vaporization to the atoms to be $\Delta H^\circ_0 = 458.3 \pm 6.5$ kcal mole$^{-1}$. Using $\Delta H^\circ_0$ for Zr(g) equal to 145.5 kcal mole$^{-1}$ [74] and $\Delta H^\circ_0$ for B(g) equal to 133.0 kcal mole$^{-1}$ [75], they calculated $\Delta H^\circ_{f0}$, for $ZrB_{1.906} = -59.3$ kcal mole$^{-1}$.

Goldstein and Trulson [77] have determined the heat of formation of zirconium diboride from vaporization studies in a mass spectrometer, obtaining $\Delta H^\circ_{f298} = -71.12$ kcal mole$^{-1}$. A similar high temperature mass spectrometric study has been done by Buchler [78] who found a value for the heat of formation of $ZrB_2$ which he describes as consistent with the data of Huber, Head and Holley [60].

Bolgar, Verkhoglyadova, and Samsonov [20] determined the vapor pressure of zirconium diboride using the Langmuir technique over the temperature range 1100° to 2000 °C. They assumed the vapor phase to be molecular $ZrB_2$, and from a second-law treatment of the data calculated the heat of vaporization to be 56.4 kcal mole$^{-1}$.

From a calorimetric study, Krestovnikov and Vendrikh [79] have reported values for the specific heat of zirconium diboride from room temperature to 800 °C, and compiled values differing by less than 10% from Maydel's equations [80] for the estimation of the heat capacity from the position of the elements in the periodic table and the heat of formation of the compound involved. Westrum and Feick [81] measured the heat capacity and tabulated the heat capacity, entropy, enthalpy, and free energy functions for zirconium diboride in the temperature range 5° to 350 °K.

Mezaki et al [18] determined the enthalpy and tabulated the heat capacity, entropy and enthalpy of zirconium diboride over the range 298° to 1200 °K. Appreciable discrepancies were reported for the temperature interval 300° to 500 °K where low and high temperature data must be connected. Prophet [82] measured the heat capacity of zirconium diboride by the rate-of-cooling method over the temperature range 1300° to 2150 °K. The heat capacity of $ZrB_2$ was also measured by Neel, Pears, and Oglesby [83] over the temperature range 533° to 2477 °K.

## 1.4 Comments and Criticism

The work of Brewer and Haraldsen [17] was probably the first major step forward in estimating the heats of formation of metallic borides. The information derived from the study is qualitative, and caution should be used in applying it, as was shown by Williams [61] who repeated some of the measurements involving $TiB_2$ and found them to be in error. The measurements involved are described in more detail in the paragraph on $TiB_2$ in Section 1.3.

Samsonov has used the vacuum thermal method to obtain pressure data at high temperatures for various metal oxide-boron carbide reactions in order to arrive at approximate heats of formation of many metal borides (See Table 1.40). It has been found to be impossible to reproduce the calculations of the heats of formation not only because of lack of pressure-temperature equilibrium data, but also because no values are given for the entropy and enthalpy data assigned to various products and reactants of the system under consideration. The value of such approximate heats of formation is thus extremely limited, despite the care which must have gone into obtaining the data necessary for calculating them. To attempt to use these data, as well as some other similar data in the Russian literature, in a critical evaluation of available information, is extremely frustrating, because there seems to be no way to correlate these values with others determined in different ways, or to modify the results originally presented, when more recent and more accurate auxiliary data become available.

TABLE 1.40

HEATS OF FORMATION OF METALLIC BORIDES DETERMINED BY SAMSONOV USING THE VACUUM THERMAL TECHNIQUE

| Metal Boride | Heat of Formation kcal $mole^{-1}$ | Reference |
|---|---|---|
| $LaB_6$ | -112.3 ±6.5 | [51] |
| $SrB_6$ | - 50.4 | [58] |
| $CrB_2$ | - 19 | [47] |
| $CeB_6$ | - 81 ±16 | [44] |
| $YB_6$ | - 24 | [73] |
| $ZrB_2$ | - 63.1 | [47] |
| $HfB_2$ | - 72.4 | [50] |

As an illustration of this situation we may examine a paper in which Samsonov [23] reported investigating the reduction of titania with carbon and boron carbide and from pressure measurements recorded as a function of time at several temperatures. He used his data to determine an equilibrium constant. The following reactions were involved in the study:

$$2TiO_2 + B_4C + C \rightleftarrows Ti_2O_3 + B_4C + CO$$

$$Ti_2O_3 + B_4C + C \rightleftarrows 2TiO + B_4C + CO$$

$$2TiO + B_4C + C \rightleftarrows 2TiB_2 + 2CO$$

The equilibrium constant was a function of the CO pressure since it was the only volatile product. It was assumed that at a given temperature a break in the pressure-time curve came when a reaction took place liberating CO. The pressure at the break in the curve denoting the commencement of a reaction was assumed to be the equilibrium pressure and proportional to the equilibrium constant.

We have not been able to reproduce the value $\Delta H^{\circ}_{f298} = -70.04$ kcal mole$^{-1}$ calculated by Samsonov for $TiB_2$, using the information given in the paper, and therefore are not sure we understand the process by which the calculation was made. In other papers involving vapor pressure measurements, the pressure data upon which the heat of reaction was based are not given, and so cannot be correlated with other data on the same reaction, or be correlated using another theoretical approach.

Samsonov [47] used an empirical relationship found in Kubaschewsky and Evans [48] to calculate heats of formation of several metal borides. (See Table 1.41). The relation is between the change in molar volume on forming a compound from its elements and the heat of formation of the compound. The percent change in molar volume, defined as follows, is used:

$$\Delta V = 100 \frac{(MV - \Sigma AV)}{\Sigma AV}$$

where $\Delta V$ is the percent change in molar volume on formation of the compound, MV is the molar volume of the compound and $\Sigma AV$ is the sum of the atomic volumes of the elements. If $\Delta V$ and $\Delta H_f$ are known for some compounds of a given crystal class, then $\Delta H_f$ can be calculated approximately for a compound for which only $\Delta V$ is known. By a slight elaboration, the method can be applied to correlate the data on compounds of different crystal classes also.

TABLE 1.41

HEATS OF FORMATION OF METALLIC BORIDES DETERMINED BY SAMSONOV [47] USING AN EMPIRICAL RELATION BETWEEN THE HEAT OF FORMATION AND THE CHANGE IN MOLAR VOLUME ON FORMING A COMPOUND FROM ITS ELEMENTS

| Metal Boride | Heat of Formation kcal $mole^{-1}$ |
|---|---|
| $TiB_2$ | -73 |
| $ZrB_2$ | -65 |
| $VB_2$ | -62 |
| $TaB_2$ | -63 |
| $CrB_2$ | -47 |
| $MoB_2$ | -60 |
| $W_2B_5$ | -49 |
| $NbB_2$ | -59 |

Samsonov [47] attempted to correlate the heats of formation of borides as well as carbides and nitrides of transition metals with such factors as ionization potential of the non-metal, the number of non-metal atoms per metal atom, and the occupancy of d-orbitals of the transition metal. His results allow interpolation or extrapolation to compounds for which $\Delta Hf$ is not known. The values obtained are extremely approximate not only because the assumptions made about the relationships involved are very uncertain, but also because the correlations were based on the data of Brewer and Heraldsen [17] and earlier work by Samsonov [23], which were not very accurate. These estimates of the heats of formation are shown in Table 1.42.

TABLE 1.42

HEATS OF FORMATION OF TRANSITION METAL BORIDES ESTIMATED BY SAMSONOV [47] FROM ELECTRONIC PROPERTIES

| Metal Boride | Heat of Formation kcal $mole^{-1}$ |
|---|---|
| $ZrB_2$ | -60 |
| $VB_2$ | -24 |
| $NbB_2$ | -33.5 |
| $TaB_2$ | -45.0 |

It is interesting to note the contrasting results obtained in the vaporization of borides by Bolgar, Verkhoglyadova, and Samsonov [20] on the one hand, and by Schissel and Trulson [63], Leitnaker, Bowman and Gilles [60], and Schissel and Williams [64] on the other hand. Their results differ strikingly in the nature of the vapor phases and the heats of vaporization observed. The vapor pressure measurements covered temperature ranges that were largely different, but some overlap did occur. Bolgar, Verkhoglyadova, and Samsonov [20] determined the vapor pressures and heats of vaporization of fourteen refractory compounds among which were $SrB_6$, $TiB_2$, $ZrB_2$, $CrB_2$, and $AlB_{12}$. Of the refractory compounds studied, all were reported to vaporize to molecular species with the exception of $AlB_{12}$ which dissociated yielding aluminum as one of the products. The substances were studied over the temperature range 1100° to 2000 °C using the Langmuir technique. The results they reported are listed in Table 1.43.

TABLE 1.43

HEATS OF VAPORIZATION OF BORIDES
BY BOLGAR, VERKHOGLYADOVA AND SAMSONOV [20]

| Metal Boride | Heat of Vaporization kcal mole$^{-1}$ |
|---|---|
| $SrB_6$ | 97.9 |
| $TiB_2$ | 45.7 |
| $ZrB_2$ | 56.4 |
| $CrB_2$ | 41.2 |
| $AlB_{12}$ | 45.7 |

Schissel and Trulson [63] determined the heat of vaporization of titanium diboride using a mass spectrometer with Knudsen cells in the temperature range 2000° to 2500 °K. They calculated the heat of vaporization at 298 °K for $TiB_2$ to be 430 kcal mole$^{-1}$. Leitnaker, Bowman and Gilles [60] measured the vapor pressure of zirconium over zirconium diboride using the Knudsen method in the range 2150° to 2475 °K. Using the third-law treatment of their data they calculated the heat of vaporization to be 458.3 ±6.5 kcal mole$^{-1}$. Leitnaker et al. cite the following as evidence for believing no gaseous $ZrB_2$ exists over the temperature range studied. First, agreement between the second-law and third-law calculations was poorer if gaseous $ZrB_2$ was assumed than if only gaseous atoms were assumed to be present. Secondly, their tests showed that significant amounts of Zr and B vapor were present over zirconium diboride. Thirdly, a spectrogram of an arc using $ZrB_2$ as both anode and cathode was taken in a helium atmosphere. Lines of both

Zr and B could be identified, but no prominent band structure could be seen. Lastly, the work of Schissel and Williams [64] on the vaporization of titanium diboride indicated there was no gaseous $TiB_2$ present in the system. It seems reasonable to extend these results to the Zr-B system.

1.5 Heat of Formation Data on Metallic Borides

| Boride Phase | $\Delta H^{o}_{f298^{o}}$ kcal mole$^{-1}$ | Reference |
|---|---|---|
| $AlB_2$ | (-80) | [19] |
| $B_4C$ | +66.0 | [23,24,25] |
| | +48.12 | [26,27] |
| | -13.8 | [28] |
| | -12.2 | [27] |
| BN | -60.7 | [30] |
| | -60.8 | [31] |
| | -59.51 | [32] |
| | -60.52 | [33] |
| | -59.8 | [34] |
| | -60 | [35] |
| | -61 | [36,37] |
| | -29.7 | [38] |
| BP | -19.9 | [41] |
| $B_{13}P_2$ | -31 | [41,42] |
| $CeB_6$ | (-84) | [17] |
| | -81 | [44] |
| CrB | (-15) | [17] |
| $CrB_2$ | (<-30) | [17] |
| | (-19) | [47] |
| | (-47) | [47] |
| $HfB_2$ | -74.2 | [50] |
| $LaB_6$ | -112.3 | [51] |
| $Mo_2B$ | -25.5 | [53] |
| $Mo_3B_2$ | -41.9 | [53] |
| $MoB_{0.96}$ | -16.1 | [53] |
| $MoB_{1.06}$ | -16.6 | [53] |
| $MoB_{2.14}$ | -19.7 | [53] |
| $MoB_{2.33}$ | -20.0 | [53] |
| $NbB_2$ | (<-37) | [17] |
| | (-59) | [47] |
| | (-33.5) | [47] |
| | -42 | [55] |
| $SiB_6$ | -7.0 | [57] |
| $SrB_6$ | -50.4 | [58] |
| $TaB_2$ | (<-45) | [17] |
| $TaB_2$ | -45.4 to -103.4 | [59] |

| Boride Phase | $\Delta H^{\circ}_{f298^{\circ}}$ kcal mole$^{-1}$ | Reference |
|---|---|---|
| $Ta_{2.4}B$ | -38.4 to -69.4 | [59] |
| $Ta_{1.6}B$ | -38.4 to -69.4 | [59] |
| TaB | -38.4 to -69.4 | [59] |
| $TaB_2$ | (-63) | [47] |
| | (-45) | [47] |
| $ThB_4$ | (<-54) | [17] |
| $ThB_6$ | (<-66) | [17] |
| $Ti_2B_5$ | (-105) | [17] |
| $TiB_2$ | (-72) | [17] |
| | -70.04 | [23] |
| | (-73) | [47] |
| | -84 | [61] |
| | -50 | [62] |
| | -32 | [64] |
| | -66.85 | [65] |
| $W_2B$ | -20 to -28 | [17] |
| | -20 to -26 | [59] |
| WB | (-12 to -22) | [17] |
| $W_2B_5$ | (-25 to -45) | [17] |
| $VB_2$ | (-62) | [47] |
| | (-24) | [47] |
| $YB_6$ | -24 | [73] |
| $ZrB_{12}$ | (<-120) | [17] |
| $ZrB_2$ | (-78) | [17] |
| | -75.02 | [65] |
| | -76.7 | [60] |
| | -71.5 | [76] |
| | -63.1 | [47] |
| | (-65) | [47] |
| | (-60) | [47] |
| ($\Delta H^{\circ}_{f0^{\circ}}$) | -59.3 | [60] |
| | -71.12 | [77] |

Values in parentheses are estimates.

## 1.6 References


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## 2.0 An Investigation of Some Zirconium Boride Preparations

### 2.1 Introduction

In studying the boron-zirconium system investigators at the Atlantic Research Corporation performed density determinations on four zirconium boride preparations made for them by a commercial supplier of boron compounds. Results of this study showed the preparations to have unusually high densities for the compositions attributed to them by the supplier. The anomalous density data presented circumstantial evidence for the existence of a higher boride, for which the formula $ZrB_{28}$ was suggested, and for which a high heat of combustion per unit volume might be expected. Data obtained from an Atlantic Research Corporation graph of density vs composition are shown in Table 2.10.

TABLE 2.10

COMPOSITION-DENSITY DATA SUPPLIED WITH ZIRCONIUM BORIDE PREPARATIONS

| Preparation No. | Reported Composition[a] (percent by weight) | | | Density[b] ($g\ cm^{-3}$) |
|---|---|---|---|---|
| | B | Zr | Total | |
| I | 70 | 30 | 100 | 5.84 |
| II | 85 | 15 | 100 | 4.79 |
| III | 78 | 22 | 100 | 5.52 |
| IV | 80 | 20 | 100 | 5.43 |

[a]Reported by the supplier.

[b]Reported by Atlantic Research Corporation.

The four zirconium boride preparations, which consisted of powders of -100 mesh particle size, were given to us by E. A. DeZubay and E. Schmidt of the Atlantic Research Corporation. We undertook to carry out tests to establish the possibility of the existence of a compound such as $ZrB_{28}$ having a high energy of combustion per unit volume.

The following studies were performed to characterize the preparations: (1) x-ray diffraction analysis, (2) wet chemical analysis for total zirconium and total boron content, and (3) density determinations. In addition to the characterization studies the heats of combustion in fluorine were determined.

## 2.2 Characterization of Zirconium Boride Preparations

X-ray studies were carried out by the National Bureau of Standards (NBS) Crystallography Section, who reported finding $ZrB_2$, $ZrB_{12}$ and an unknown phase (or phases) in each preparation. From inpsection of the X-ray powder patterns rough estimates of the relative amounts of the components were made, assuming line intensity to be a function of the fraction of a component in the preparation. Attempts to identify the unknown phase(s), by comparison of the X-ray patterns with known patterns of $ZrO_2$, $B_2O_3$, Zr, and B, did not result in a clear-cut assignment. Qualitative results of the X-ray diffraction analyses are given in Table 2.20.

TABLE 2.20

COMPONENTS OF ZIRCONIUM BORIDE PREPARATIONS DETERMINED BY X-RAY DIFFRACTION ANALYSIS AT NBS

| Preparation No. | Relative amounts of phases present (estimated on the basis of line intensity) |
|---|---|
| I | Mostly $ZrB_2$; moderate amount $ZrB_{12}$; least unknown phase. |
| II | Mostly unknown phase; about equal smaller amounts of $ZrB_2$ and $ZrB_{12}$. |
| III | Mostly $ZrB_2$; moderate amount $ZrB_{12}$; least unknown phase. |
| IV | Moderate and about equal amounts of $ZrB_2$ and $ZrB_{12}$; least unknown phase. |

Wet chemical analyses for total zirconium and total boron were performed by the NBS Applied Analytical Research Section. Density determinations were made by the NBS Volumetry and Densimetry Section. The results of these determinations are summarized in Table 2.22.

TABLE 2.21

COMPOSITION AND DENSITY OF ZIRCONIUM BORIDE PREPARATIONS DETERMINED AT NBS

| Preparation No. | Composition (percent by weight) | | | Density g cm$^{-3}$ |
|---|---|---|---|---|
| | B | Zr | Total | |
| I | 25.4 | 61.6 | 87.0 | 4.898 |
| II | 34.6 | 52.4 | 87.0 | 4.444 |
| III | 23.9 | 63.6 | 87.5 | 5.091 |
| IV | 30.5 | 54.5 | 85.0 | 5.555 |

A significant difference exists in the percentages of zirconium and boron in the preparations as stated by the supplier of the samples (Table 2.10), and as found by the NBS Applied Analytical Research Section. The zirconium and boron percentages do not add up to 100%, but to about 87%, implying the presence of substantial amounts of other elements. This finding is in keeping with the X-ray diffraction analysis data which indicate the presence of an unknown phase.

Comparison of the density data in Tables 2.10 and 2.21 shows that the agreement between determinations at the Atlantic Research Corporation and at the NBS is reasonably satisfactory.

The zirconium boride preparations were analyzed for metallic impurities by the NBS Spectrochemistry Section. The results of the spectrographic analysis are given in Table 2.22. Inspection of Table 2.22 reveals that metallic impurities are present in the preparations to a total of about one percent or less. The total boron and zirconium content plus the metallic impurities add up to less than 90%. The remainder presumably is non-metals, probably oxygen, nitrogen, or carbon.

TABLE 2.22

METALLIC IMPURITIES IN THE ZIRCONIUM BORIDE PREPARATIONS

| Preparation No. | Concentration Level of Impurities (Percent | | | |
|---|---|---|---|---|
| | 0.1 to 1.0 | 0.01 to 0.1 | 0.001 to 0.01 | Trace |
| I | W | Si,Ca,Cu | Al,Cr,Ti,Ni,Mg,Fe,Mn | Be,Ag |
| II | W | Si,Ca,Cu,Fe | Al,Cr,Ti,Ni,Mg,Mn | Be,Ag |
| III | W | Si,Ca,Cu | Al,Cr,Ti,Ni,Mg,Fe | Be,Ag,Mn |
| IV | W | Si,Ca,Cu,Fe | Al,Cr,Ti,Ni | Be,Ag,Mn |

Because of the unknown phase (or phases) found in the X-ray study, the hypothetical compound $ZrB_{28}$ was not completely precluded. However, the actual compositions of the preparations as observed in our laboratories give an approximate linear density-composition plot, and hence the principal basis for supposition of the existence of $ZrB_{28}$ has been removed. It is not necessary to assume any unusual properties or new substances in order to account for the observed compositions and densities of the preparations.

## 2.3 Heats of Combustion in Fluorine of the Zirconium Boride Preparations

Because the principal concern in this investigation was in a boride of high energy of combustion per unit volume, and because the analyses found in our laboratories were so much at variance with previously indicated compositions, we felt that it was desirable to determine at least approximately the heats of combustion of these preparations in fluorine.

The calorimeter combustion bomb, fluorine manifold, temperature measuring apparatus, and general techniques and procedures were essentially the same as those used in the fluorine combustion studies on $AlB_2$ and $\alpha$-$AlB_{12}$ which are described in more detail in Section 5.

A sample of Teflon was burned in fluorine to obtain an approximate energy equivalent for the calorimetric system. The heat of combustion of Teflon in fluorine had been determined in a previous investigation [1].

About 0.5 g of the zirconium boride sample was mixed with 1.7 g of powdered Teflon, the mixture pressed into a pellet and burned in fluorine at a pressure of 300 psi in a nickel combustion bomb. After removing the product gases and excess fluorine from the bomb, following an experiment, a solid, white, hygroscopic residue was found clinging to the inner surfaces of the bomb. This was assumed to be zirconium tetrafluoride. The absence of any black residue in the white powder indicated that the reaction had gone essentially to completion. The heat measurements on the four preparations are summarized in Table 2.30.

TABLE 2.30

HEATS OF COMBUSTION OF ZIRCONIUM BORIDE PREPARATIONS IN FLUORINE

| Preparation No. | Composition (percent by weight) | | Heat of Combustion | | |
|---|---|---|---|---|---|
| | | | Calculated | Observed | |
| | B | Zr | kcal $g^{-1}$ | kcal $g^{-1}$ | kcal $cm^{-3}$ |
| I | 25.4 | 61.6 | - 9.34 | - 8.5 | -41.6 |
| II | 34.6 | 52.4 | -11.27 | -10.5 | -46.7 |
| III | 23.9 | 63.3 | - 9.14 | - 8.5 | -43.3 |
| IV | 30.5 | 54.5 | -10.45 | - 9.9 | -55.0 |
| - | 100.0 | | -25.0 [2] | | |
| - | | 100.0 | - 5.0 [3] | | |

Since only a single heat measurement was made on each sample, the heats of combustion determined must be considered as approximate. The observed heats of combustion shown in Table 2.30 fall between the heats of combustion of elemental boron and elemental zirconium. The calculated heats of combustion in Table 2.30 represent the heat that would be evolved when an uncombined mixture containing elemental boron and zirconium in the same percentages as in the preparation, is burned in fluorine. The presence of an inert uncombined element in the preparation is assumed, in order to bring its constituents up to 100%. The calculated heats of combustion are larger (more negative) than those determined experimentally. The difference is easily attributed, in a qualitative way, to the fact that another element present in the samples is probably combined with some of the boron or zirconium, in a compound having strongly negative heat of formation. The energy difference due to such an effect could be so large and is so uncertain that it obscures the effect of the binding of Zr with B.

Because of the large amount of the unknown phase present in the sample (approximately 10 to 13%), and because the amounts of $ZrB_2$ and $ZrB_{12}$ in the samples are known only roughly, it is not possible to estimate the heat of combustion or heat of formation of any of the zirconium borides.

The combustion data are consistent with the wet chemical analyses and the X-ray analyses in the sense that an approximate value for the energy of combustion can be calculated from the analysis. They are in agreement in indicating much lower boron contents than were initially postulated for the four preparations. While the densities of the preparations were confirmed, no evidence is found for the existence of a compound having the formula $ZrB_{28}$, or for a formulation having an unusually high heat of combustion per unit volume.

## 2.4 References


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## 3.0 Procurement and Preparation of Metallic Borides and Boron

### 3.1 Introduction

For the combustion calorimetry tasks to be carried out, samples of pure metal borides were required. When determined by combustion calorimetry, the heat of formation of a boride will be a small difference between the heats of combustion of the uncombined elements and the compound. For this reason the sample of the compound must be as pure as feasible, and carefully analyzed in order that lack of knowledge of the sample itself will not introduce uncertainties so large that they render the experiment valueless. The preparation (Section 3) and analysis (Section 4) of the materials to be studied, therefore, is a primary concern in this type of calorimetric study. Several borides of aluminum, the diborides of titanium and zirconium, and elemental boron were obtained as special preparations for this work. The Carborundum Company was interested in borides for its own research program and agreed to prepare several compounds for the National Bureau of Standards. Because some development of the methods of preparation was to be required, the task was undertaken on a cost sharing basis. The preparation and characterization of the aluminum titanium and zirconium borides was carried out by V. I. Matkovich and J. Economy of the Carborundum Company.

Boron was obtained from the Eagle-Picher Company, Miami, Oklahoma.

### 3.2 Aluminum Borides

The aluminum borides that have been described in the literature are listed in Table 3.20, together with citations from the literature in which their characterization has been presented.

TABLE 3.20

BORIDES OF ALUMINUM

| Phase | Crystal system | Reference |
|---|---|---|
| $AlB_2$ | hexagonal | [1,2] |
| $AlB_4$ | - | [3] |
| $AlB_{10}$ | orthorhombic | [4,5,7] |
| $\alpha$-$AlB_{12}$ | tetragonal (pseudocubic) | [4,5] |
| $\beta$-$AlB_{12}$ | orthorhombic (pseudotetragonal) | [4,5] |
| $\gamma$-$AlB_{12}$ | orthorhombic | [5,6] |

At the outset of the program all of the compounds were considered to be well established except $AlB_4$. During the course of the work it became evident that there was a question of the existence not only of $AlB_4$ but of $AlB_{10}$ and $\beta$-$AlB_{12}$ as well. Alternative compounds, $AlC_4B_{25}$ and $Al_2CB_{32}$, were prepared and characterized. These are stated by the supplier to be the phases formerly described as $AlB_{10}$ and $\beta$-$AlB_{12}$, respectively, and the formulas are stated to be more accurate representations of the phases than are the formulas containing no carbon.

The procedures used by Matkovich [8] in the preparation of the aluminum borides will be briefly outlined in order to provide a complete characterization of the materials used in this study.

The aluminum borides were prepared by mixing excess aluminum with boron and heating the mixture by induction in an air-free, dry, argon atmosphere. Boron nitride crucibles were used when temperatures above 1400 °C were required, and zirconia crucibles for preparations at lower temperatures. The phase produced was controlled principally by the weight ratio of aluminum to boron, the temperature to which the mixture was heated, and the rate of cooling of the product.

In order to obtain the crystallographic phases described for $\beta$-$AlB_{12}$ and $AlB_{10}$ [4], it was found necessary to add graphite to the mixture. In the absence of graphite these two phases were not found. The formulas proposed by Matkovich [8] for these compounds are $Al_2CB_{32}$ (formerly $\beta$-$AlB_{12}$) and $AlC_4B_{25}$ (formerly $AlB_{10}$).

The proportions of aluminum and boron used in the preparation of the various aluminum borides and the temperatures at which they were formed are listed in Table 3.21.

TABLE 3.21

CONDITIONS FOR PREPARATION OF ALUMINUM BORIDES

| Boride Phase | Weight Ratio Al/B | Temperature °C |
|---|---|---|
| $\alpha$-$AlB_{12}$ | 4 | 1700 |
| $\gamma$-$AlB_{12}$ | 20 | 1400 |
| $Al_2CB_{32}$ ($\beta$-$AlB_{12}$) | 20 | 1400 |
| $AlC_4B_{25}$ ($AlB_{10}$) | 20 | 1400 |
| $AlB_2$ | 80 | 1200 |

Oxides of aluminum and boron were separated by gravity from the melts. The melts were quenched at the rate of 100 °C per hour to obtain the desired phase. Rapid cooling in the preparation of $\alpha$-$AlB_{12}$ was important to exclude $\gamma$-$AlB_{12}$. Excess aluminum was removed from the final mixtures by treatment with acid. However, $AlB_2$ is dissolved, reducing the yield. In our opinion, aluminum is apparently also preferentially dissolved from $AlB_2$, leaving a non-stoichiometric compound with an aluminum deficiency.

For a more detailed account of the crystallography and preparative procedures of the aluminum borides, the reader is referred to a paper "Presence of Carbon in Aluminum Borides", by V. I. Matkovich and J. Economy, to be published in the near future. See also [9]. The description and analysis of the samples received is given in Section 4.

### 3.3 Titanium and Zirconium Borides

The titanium and zirconium borides that have been described in the literature are listed in Table 3.30, together with a citation of the literature in which their characterization has been described.

TABLE 3.30

BORIDES OF TITANIUM AND ZIRCONIUM

| Phase | Crystal System | Reference |
|---|---|---|
| $Ti_2B$ | tetragonal | [10,11,12] |
| TiB | orthorhombic | [12,13,14] |
| $TiB_2$ | hexagonal | [13,14,15] |
| $Ti_2B_5$ | hexagonal | [11,16] |
| ZrB | cubic | [14,17,18] |
| $ZrB_2$ | hexagonal | [14,18] |
| $ZrB_{12}$ | cubic | [17,19] |

Titanium diboride was prepared by electrolysis, using graphite electrodes and a fused salt electrolyte composed of KCl, $KBF_4$ and $K_2TiF_6$. Zirconium diboride was prepared in an analogous manner, using $K_2ZrF_6$ instead of $K_2TiF_6$ in the electrolyte.

Several problems arose in the preparation of zirconium dodecaboride which is prepared in much the same way as the aluminum borides. Problems of finding a suitable crucible and a method of separating $ZrB_{12}$ from $ZrB_2$ were not resolved, and so $ZrB_{12}$ was not prepared under the program described in this report.

Fifty grams of zirconium diboride and 30 grams of titanium diboride were supplied in the form of -100 mesh gray powder by the Carborundum Company. The analyses supplied with the samples are shown in Table 3.31. The zirconium to boron ratio submitted corresponds to the formula $ZrB_{1.72}$; the titanium to boron ratio corresponds to $TiB_{1.95}$.

TABLE 3.31

ANALYSES OF ZIRCONIUM AND TITANIUM DIBORIDES

| A. Zirconium Diboride | | |
|---|---|---|
| Element | Composition (percent by weight) | |
| | Theoretical | Determined[a] |
| Zr | 80.839 | 81.20 |
| B | 19.161 | 18.29 |
| C | | 0.14 |
| Si | | 0.17 |
| Fe | | < 0.1 |
| Total | 100.000 | 99.90 |

| B. Titanium Diboride | | |
|---|---|---|
| Element | Composition (percent by weight) | |
| | Theoretical | Determined[a] |
| Ti | 68.899 | 69.19 |
| B | 31.101 | 30.27 |
| C | | 0.3 |
| Si | | 0.15 |
| Fe | | 0.18 |
| Total | 100.000 | 100.09 |

a. Determined by the Carborundum Company

## 3.4 Elemental Boron

A ten gram sample of -100 mesh crystals of high purity boron of the β-rhombohedral phase was received from the Eagle-Picher Company. It was prepared by the hydrogen reduction of boron tribromide on a substrate of zone refined boron, as described by Starks and Bedford [20]. Emission spectrographic analysis showed 3 ppm. Si and 7 ppm. Cu. Carbon analysis by the method of Kuo, et al. [21] showed 500 ppm. carbon.

## 3.5 References


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## 4.0 Characterization of the Aluminum Boride Samples

### 4.1 Aluminum Diboride

Aluminum diboride was received in four lots: sample I, 5 grams, +20 mesh; sample II, 2.8 grams, -20/+80 mesh; sample III, 26 grams, +20 mesh; sample IV, 12 grams, -20/+80 mesh. The samples consisted of thin black crystalline platelets of sizes up to several mm. in dimension, having a metallic luster.

An analysis of sample I was submitted by the supplier based on wet chemical methods for boron and aluminum. Analysis of sample III was made by the NBS Applied Analytical Research Section using wet chemical methods for boron, aluminum, carbon, nitrogen and metallic impurities. A determination of the oxygen content in sample III was made using neutron activation analysis by General Atomic, San Diego, California. Spectroscopic analyses were made of samples I and II by the Carborundum Company and of sample III by the NBS Spectrochemistry Section. The analyses are summarized in Table 4.1, in comparison with the theoretical composition of $AlB_2$. Spectroscopic values are given in parentheses. Sample II showed definitely higher amounts than sample I of the major metallic contaminants Cu and Fe, as determined by the Carborundum Company. Sample III, which was comparable in crystal size to sample I exhibited a similar analysis for minor constituents, so far as the comparison was made. However, comparison of the total aluminum and total boron in $AlB_2$ as found by our Applied Analytical Research Section and by the Carborundum Company analysts reveals a relatively large discrepancy. In an attempt to resolve this discrepancy, a small amount of sample III and copies of the analytical procedures used in the NBS Applied Analytical Research Section on the aluminum borides were sent to the Carborundum Company so that a comparison of procedures could be made. The Carborundum Company later informed us that the NBS analyses on aluminum diboride were correct and that the error lay in some approximations used in their analytical procedures. The fact that the total boron analysis was greater than the theoretical value is ascribed to lattice vacancies and/or boron atoms in aluminum positions.

TABLE 4.1

ANALYSES OF ALUMINUM DIBORIDE

| Element | Composition (percent by Weight) | | | | |
|---|---|---|---|---|---|
| | | Supplier's Analysis | | NBS Analysis | |
| | Theoretical | Sample I | Sample II | Sample III | |
| B | 44.487 | 44.29 | | 47.04 | |
| Al | 55.513 | 54.74 | | 53.00 | |
| C | | | | .08 | |
| N | | | | .30 | |
| O | | | | 1.0 a | |
| Cu | | (0.1) | (0.5) | 0.075 | (0.001-0.01) |
| Fe | | (0.2) | (0.4) | 0.025 | (0.001-0.01) |
| Si | | (0.07) | (0.007) | 0.026 | (0.001-0.01) |
| Mg | | (0.02) | (0.04) | 0.024 | (0.001-0.01) |
| Ca | | (0.03) | (0.01) | 0.013 | (trace) |
| Mn | | (0.02) | (0.02) | 0.01 | (0.001-0.01) |
| Ag | | | | | (trace) |
| Cr | | (0.03) | (0.02) | | (trace) |
| Pb | | | | | (trace) |
| Sn | | (<0.005) | (0.04) | | (trace) |
| Ti | | (<0.005) | (<0.005) | | |
| Zr | | (0.01) | (0.01) | | |
| V | | (0.005) | (0.005) | | |
| Total | 100.00 | | | 101.593 | |

a. Determined by General Atomic, San Diego, California.

An X-ray powder pattern obtained for aluminum diboride by the NBS Crystallography Section is in good agreement with data available on this phase. [1] The pattern gives no evidence for the presence of any other phase. The lattice constants found, a = 3.005A and c = 3.250A, are in good agreement with the literature cited.

## 4.2 α Aluminum Dodecaboride

Two samples of $\alpha$-$AlB_{12}$ were received: Sample I, 25 g, granular crystals ranging from 0.5 to 2.0 mm in diameter; sample II, 46 g, 200 mesh powder. Several analyses were performed, which are summarized in Table 4.2. The supplier provided an analysis of sample I which showed the major impurities to be 0.2% oxygen and 0.2% carbon. Trace amounts of chromium, magnesium, and titanium were observed spectroscopically at levels of 0.05% or less. In Table 4.2, results of spectroscopic analysis are shown in parentheses. The aluminum content was found to be 16.17%, which is somewhat lower than the theoretical value of 17.217%. The boron analysis ranged from 81.2 to 83.2%, compared with the theoretical value of 82.78%. From these figures the boron to aluminum atomic ratio is 12.5 to 12.8, rather than the stoichiometric value of 12.

TABLE 4.2

ANALYSES OF α-ALUMINUM DODECABORIDE

| Element | Composition (percent by weight) | | | | |
|---|---|---|---|---|---|
| | | Supplier's Analysis | | NBS Analysis | |
| | Theoretical | Sample I | Sample II | Sample I | Sample II |
| B | 82.783 | 81.2 - 83.2 | | 82.2 | 81.5 |
| Al | 17.217 | 16.17 | | 17.10 | 17.01 |
| Ca | | | | 0.025(0.01-0.1) | 0.018(0.01-01) |
| Mg | | (< .05) | | 0.15(0.1-1.0) | 0.15 (0.1-1.0) |
| Si | | | | 0.14(0.01-0.1) | 0.05(0.1-1.0) |
| C | | 0.2 | | 0.18 | 0.11 |
| N | | | | - | 0.0 a |
| O | | 0.2 | 0.5 - 0.7 | - | 1.13 a |
| Fe | | | | | (0.01-0.1) |
| Zr | | | | | |
| Ti | | (< .05) | | | (0.001-0.01) |
| Cr | | (< .05 | | | (0.001-0.01) |
| Mn | | | | (trace) | (0.001-0.01) |
| Zr | | | | (0.001-0.01) | (0.001-0.01) |
| Cu | | | | | (0.001-0.01) |
| Total | 100.00 | 97.77 - 99.77 | | 99.795 | 100.138 |

a Determined by General Atomic, San Diego, California.

Sample II was obtained by grinding the granular crystals. After the grinding procedures the oxygen content was found to have increased to 0.5 - 0.7%. Samples I and II were analyzed spectroscopically for metals by the NBS Spectrochemistry Section and using wet chemical methods for boron, aluminum, carbon, and metallic impurities by the NBS Applied Analytical Research Section. Oxygen and nitrogen were determined in sample II by General Atomic, San Diego, California.

X-ray diffraction analyses of the α-$AlB_{12}$ powder performed by the Crystallography Section identified the unit cell as tetragonal with a = 10.162A and c = 14.26A. These data were in agreement with the cell assignment and lattice parameters previously determined [2].

Overall agreement of the results of the analysis on the $\alpha$-$AlB_{12}$ samples obtained from the Carborundum Company and performed in the NBS laboratories is good, but certain differences are evident. Although the total boron and aluminum content of sample I is about the same in the two analyses, 99.4% compared to 99.3%, the percent aluminum found by Carborundum Company is lower, 16.17%, than that found by NBS 17.10%. On the basis of the NBS analytical data, the boron to aluminum ratios for both the crystals and the powder appear to be in excellent agreement with the theoretical value, 12.00. The data for the $\alpha$-$AlB_{12}$ crystals gives a B/Al ratio of 12.00, while the $\alpha$-$AlB_{12}$ powder gives a B/Al ratio of 11.96.

Spectrographic analysis performed in the NBS laboratories showed no titanium or chromium in the $\alpha$-$AlB_{12}$ crystals, while the Carborundum Company reported their presence at a level $< 0.05\%$. We found magnesium present from 0.1 to 1.0% while they reported it at $< 0.05\%$. Our analysis shows calcium and silicon present at the 0.01 to 0.1% level, while no mention is reported of their presence by Carborundum. It appears that the grinding and sieving process contaminated the sample. These steps seem to have introduced Fe, and Cu, and possibly Ti and Cr.

## 4.3 $\gamma$-Aluminum Dodecaboride

Two samples of $\gamma$-$AlB_{12}$ were received: sample I, 63.6 grams, crystals several mm. in diameter; sample II, 49.2 grams, -80 mesh granules crushed from the large crystals. The large crystals are black and have a metallic luster, while the granules appear reddish-brown. According to the technical staff at the Carborundum Company in charge of supplying these materials, it is doubtful whether the pure $\gamma$-phase can exist without about 10% of the $\alpha$-phase present. The $\gamma$-$AlB_{12}$ phase appears to be syntactically intergrown with the $\alpha$-$AlB_{12}$ phase.

The Carborundum Company did not supply any analytical data with the $\gamma$-$AlB_{12}$ sample because it was not a single phase material.

Analyses were made using wet chemical methods for B, Al, C and traces of metallic impurities by the NBS Applied Analytical Research Section. Oxygen and nitrogen were determined on sample I by General Atomic, San Diego, California, using neutron activation analysis. The analyses are summarized in Table 4.3. No explanation is known for the large deviation from complete mass balance. The X-ray powder pattern of the $\gamma$-$AlB_{12}$ is indistinguishable from that of the $\alpha$-$AlB_{12}$.

TABLE 4.3

ANALYSES OF α-ALUMINUM DODECABORIDE

| Element | Composition (percent by weight) | | |
|---|---|---|---|
| | | NBS Analysis | |
| | Theoretical | Sample I | Sample II |
| B | 82.783 | 80.55 | 80.71 |
| Al | 17.217 | 16.35 | 16.03 |
| C | | 0.07 | 0.07 |
| N | | | 0.00 a |
| O | | | 0.36 a |
| Mg | | 0.095 | 0.088 |
| Ca | | 0.011 | 0.007 |
| Fe | | | 0.005 |
| Total | 100.00 | 97.16 | 97.270 |

a Determined by General Atomic, San Diego, California

## 4.4 $Al_2CB_{32}$ (β-Aluminum Dodecaboride)

Two samples of a compound having approximately the composition $Al_2CB_{32}$ were received from the Carborundum Company; sample I, 11.0 g of crystals having dimensions of several mm, and sample II, 13.0 g of powder. The powder is dark yellow in color while the crystals are light-to-medium brown and lustrous. This compound was obtained in efforts to prepare β-$AlB_{12}$ [3,4]. The supplier states that the so called β-aluminum dodecaboride does not exist without the presence of about three percent carbon, and that the true stoichiometry is $Al_2CB_{32}$. This claim is supported by the analyses, which are summarized in Table 4.4. The Carborundum Company supplied an analysis which is in reasonably good agreement with that obtained using wet chemical methods in the NBS Applied Analytical Research Section. Oxygen and nitrogen in sample II were determined for NBS by General Atomic, San Diego, California, using neutron activation analysis. No X-ray study was made of this material.

TABLE 4.4

ANALYSES OF $Al_2CB_{32}$ (β-ALUMINUM DODECABORIDE)

| Element | Composition (percent by weight) | | | |
|---|---|---|---|---|
| | | Carborundum Co. | NBS | |
| | Theoretical (for $Al_2CB_{32}$) | Sample I | Sample I | Sample II |
| B | 83.984 | 83.35 | 83.27 | 83.36 |
| Al | 13.100 | 13.05 | 12.91 | 12.69 |
| C | 2.916 | 3.00 | 3.10 | 3.10 |
| O | | 0.31 | - | 0.46 a |
| N | | 0.19 | - | 0.39 a |
| Mg | | | | 0.075 |
| Si | | | | 0.008 |
| Totals | | 99.90 | 99.28 | 100.083 |

a Determined by General Atomic, San Diego, California

## 4.5 $AlC_4B_{25}$ (Aluminum Decaboride)

A sample of a compound having approximately the composition $AlC_4B_{25}$ was received from the Carborundum Company: sample I, 12 g of - 100 mesh black lustrous powder. This compound was identified by the supplier as the phase previously designated as $AlB_{10}$ [3,4,5]. It has incorporated in it about 14 percent carbon. The Carborundum Company supplied an analysis for boron aluminum, and carbon. No wet chemical analysis for these elements nor an X-ray examination were carried out at the National Bureau of Standards. However, General Atomic, San Diego, California, made a determination of oxygen and nitrogen using neutron activation analysis.

TABLE 4.5

ANALYSIS OF $AlC_4B_{25}$ (ALUMINUM DECABORIDE)

| Element | Composition (percent by weight) | | |
|---|---|---|---|
| | | Supplier's Analysis | NBS Analysis |
| | Theoretical | Sample I | Sample I |
| B | 78.272 | 77.34 | |
| Al | 7.814 | 7.91 | |
| C | 13.914 | 14.05 | |
| N | | | 0.57 a |
| O | | | 0.33 a |
| Total | 100.000 | 100.20 b | |

a Determined by General Atomic, San Diego, California.
b Including oxygen and nitrogen from NBS analysis.

## 4.6 References


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## 5.0 Heats of Formation of Aluminum Diboride and α-Aluminum Dodecaboride

### 5.1 Introduction

As may be seen in Section 1 of this report, thermodynamic data on the aluminum borides is not plentiful. There exists essentially no data from which the heats of formation may be calculated. Van Arkel [1] estimated the heat of formation of aluminum diboride to be -80 kcal $mole^{-1}$ by a method that he did not describe. The vapor pressure of $AlB_{12}$ was measured by Bolgar, Verkhoglyadova, and Samsonov [2] between 1100° and 2000°C. They observed aluminum in the vapor but do not state whether any other species were present in the vapor. It is therefore, not clear what relationship exists between their calculated heat of vaporization, and the heat of formation of $AlB_{12}(s)$. Interpretation of their work is further complicated by the discrepancy of about an order of magnitude in heats of vaporization of titanium diboride and zirconium diboride as reported by the above authors and as reported by Schissel and Trulson [3] and by Leitnaker, Bowman, and Gilles [4].

Because no calorimetric study had been made to determine the heats of formation of any of the borides of aluminum, this task was undertaken in our laboratories, using fluorine bomb calorimetry as the technique. A previous study of the combustion of aluminum [5] in fluorine provided a directly applicable technique for doing the calorimetry, and in addition, provided some of the essential auxiliary data necessary to calculate the heat of formation of the aluminum borides from their heats of combustion in fluorine. Combustion of the borides in oxygen forms two solid oxides as products, which may interact with one another and may retain unburned starting material mixed with them. The amount of reaction is very difficult to determine in this kind of a process. On the other hand, when aluminum boride is burned in fluorine, one of the products is gaseous, and the difficulty of carrying out a complete reaction is correspondingly decreased.

### 5.2 Materials

The aluminum diboride described in Section 4.1 as sample III, and the α-aluminum dodecaboride described as sample II were used in the combustion experiments. A further discussion of the distribution of impurities is found in Section 5.10.

The Teflon powder was a commercial preparation with particle sizes ranging from 50 to 800 microns.

The fluorine used in the final combustion experiments was a special high-purity commercial grade, with an assay of 99.85% reported by the supplier. The material was analyzed in our laboratories about a year after receipt of the fluorine. At that time an assay of 99.79% was found, using the technique of absorption of the fluorine in mercury, followed by a pressure determination and mass spectrometer analysis of the residual gas [6]. No attempt was made to purify the fluorine further, and a trap supposed to remove traces of HF was removed from the system after it was discovered that the trap was adding significant amounts of impurities.

### 5.3 Preparation of Sample Pellets

Attempts to prepare suitable pellets of $AlB_2$ or $\alpha$-$AlB_{12}$ alone were unsuccessful. The hardness and resistance to compression of these materials made the pellets too fragile for use.

Mixtures of $AlB_2$ or $\alpha$-$AlB_{12}$ with Teflon powder could be pelleted easily. Pellets made from about 300 mg. of the boride and 1.75 to 2.00 g of Teflon powder were coherent and burned almost to completion in fluorine, so these proportions were considered suitable for sample preparation.

After weighing the two powders in a suitable container, they were mixed with a needle to obtain reasonable homogeneity and transferred to the pellet die. The pellet was also weighed after preparation. A loss of weight was always observed. Part of the loss occurred from incomplete transfer of the sample from the container to the die pieces. Since it was possible to remove all of the Teflon particles from the container with the aid of the needle and a magnifying glass but not all of the boride, this part of the loss was subtracted from the mass of the aluminum boride powder. Also accounted for was the mass of the material which adhered to the die pieces as a result of the pelleting operation. It was assumed that this loss was distributed between the constituents in proportion to the original amounts of each present. The mass contribution from the amount of boride remaining in the container and the amount of pellet adhering to the die pieces was inadequate to account fully for the loss of sample materials. Similarly, it was assumed that the amount of sample unaccounted for was lost in proportion to the amounts of Teflon and aluminum boride in the pellet.

TABLE 5.30

SAMPLE LOSS IN PELLET PREPARATION

| Aluminum Boride | Sample adhering to container (mg) | Sample adhering to die pieces (mg) | Sample loss in transfer (unaccountable) (mg) | Total Loss (mg) |
|---|---|---|---|---|
| | | (Combined for $AlB_2$) | | |
| $AlB_2$ | 4.93 ±1.16 | 0.52 ±0.15 | | 5.45 ±1.10 |
| α-$AlB_{12}$ | 0.31 ±0.16 | 0.21 ±0.15 | 0.15 to 0.09 | 0.59 ±0.20 |

Table 5.30 shows the average loss of sample incurred during pellet preparation. The uncertainty given is the average deviation. The large difference in the loss of sample between $AlB_2$ and α-$AlB_{12}$ is found in a greater tendency toward adhering to the container on the part of $AlB_2$.

Samples were weighed to 0.01 mg. Buoyancy corrections were applied using 3.17 g $cm^{-3}$ [7], 2.557 g $cm^{-3}$ [7] and 2.23 g $cm^{-3}$ for the densities of $AlB_2$, α-$AlB_{12}$ and Teflon, respectively. The density of Teflon was determined in the laboratory.

## 5.4 Calorimetric Apparatus

An isothermal-jacket, stirred-water calorimeter was used, which was a modificiation of the Dickinson design similar to that used by Prosen and co-workers [8]. The calorimeter can has a volume of 4 liters. To minimize heat transfer between the motor and the calorimeter jacket an arrangement of a chain-drive system and a single motor was used for stirring both the jacket and the calorimeter water.

The motor was mounted on a Transite sheet on the jacket wall. The jacket was maintained isothermal within a range of ±0.002°C near 30°C by an electronic thermoregulator using a nickel resistance thermometer as a sensing element. A constant-flow device was used for the cooling water in order to improve temperature regulation of the calorimeter jacket.

Temperatures were measured with a G-2 Mueller Bridge in conjunction with a 25-ohm platinum resistance thermometer. The latter was immersed in the calorimeter near the calorimeter wall. Temperatures were read to 0.0001°C.

The reactions were carried out in a combustion bomb, shown in Fig. 1, which is commercially available, and was designed for service with corrosive gases such as fluorine. The bomb was fabricated from "A" nickel and has an internal volume of approximately 380 ml. A type-304 stainless steel liner

(wall thickness, 3/32 in.) was inserted into the bomb body, fitting snugly to the inner dimensions of the bomb (0.003 in. clearance). A monel pellet holder was fitted into the bottom of the liner. The holder has a recess 0.010 in. deep, in which the sample pellet was placed. The fuse wire consisted of 5 cm. of 0.003 in. diam tungsten wire. It was supported by two aluminum electrode fittings 2 in. long by 1/8 in. diam., which were suspended from the bomb head by monel rods. The mass of the fuse was about 4.4 mg. If burned completely the fuse contributed 42 j. to the combustion. For these experiments the bomb was fitted with a handle, which was used to lower the bomb into the calorimeter, and remained attached to the bomb during an experiment. In addition to the above features, the standard bomb for the fluorine combustion experiments was considered to contain 16 atm. fluorine.

A heater was used in both calibration and combustion experiments to bring the calorimeter to the desired starting temperature. It consisted of approximately 10 ohms of insulated Advance wire inside a soft copper tube which was flattened and coiled to fit the base of the combustion bomb.

### 5.5 Procedure for Loading and Emptying the Bomb

A fluorine manifold (Figure 2) was used for (1) filling and emptying the combustion bomb, (2) obtaining samples of volatile products of combustion, and (3) obtaining samples of fluorine for analysis.

The manifold consists of a series of valves, vessels, and pressure gauges by tubing and unions. The tubing was monel of 1/4 in. outside diam. and 0.035 in. wall thickness. The valves, vessels and gauges were made of monel or stainless steel and were silver soldered to the monel tubing. In some instances copper couplings were used to facilitate silver soldering a junction. Otherwise monel unions were used. Two special Bourdon gauges for fluorine service were used, one having a range 0 to 500 psi, and the other, 0 to 30 in. Hg for measuring rough vacuum. A thermocouple gauge was used to measure pressures below $10^{-1}$ mm Hg. A mechanical pump was adequate to attain the vacuum needed for working with the fluorine manifold.

The fluorine manifold system was considered to be sufficiently gastight for use if no indication of leaks was found at internal pressures of either 500 psi or 0.005 mm Hg.

To load the combustion bomb with fluorine, it was attached to the manifold by a gland-nut and cone connector. With valves F, G, M, P, R closed and valves I, K, S, U and the bomb needle valve open, the bomb was evacuated to $10^{-2}$ mm Hg. When this vacuum was attained, valves K, S, and U were closed, and fluorine was introduced into the bomb by opening the fluorine tank valve and then valves D and F. The rate of flow was regulated to allow the pressure to increase about one psi per second. When the reading on the gauge showed the pressure desired, valves F, D and the fluorine tank valve were closed. Then, after the pressure reading was taken, the bomb needle

valve was closed. If the pressure in the tank was less than the pressure desired, it was still possible to fill the bomb to this pressure by the following procedure. A small section of the line, E, was immersed in liquid nitrogen, and fluorine was condensed in it. Be allowing the condensed fluorine to evaporate and regulating the flow through valve D, the desired pressure could be obtained in the bomb. To clear fluorine from the lines after the bomb and needle valve D were closed, the bulk of the fluorine in the maniforld was admitted via valve U to the ballast tank V, from which it could be removed later. Valve U was then closed and the remaining fluorine in the lines was diluted several times with helium and released through the absorption tower, T, to the fume hood. Finally, the lines were evacuated to about 5 mm. Hg, and valve I was closed before removing the loaded bomb from the fluorine manifold.

After an experiment, the bomb was attached to the manifold in order to obtain any desired samples of gaseous combustion products and to remove the fluorine. To remove the fluorine, the procedure used for clearing the lines of fluorine was repeated in much the same manner, except that the bomb needle valve remained open until evacuation was complete. The bomb was filled with helium and re-evacuated several times, then finally filled with helium prior to opening for inspection.

## 5.6 Products of Combustion

After the combustion of aluminum boride-Teflon mixtures, a white powder was present in the bomb, mostly at the site of the combustion, but considerable amounts also clinging to the bomb walls in a finely divided state. The powder was identified by X-ray diffraction to be aluminum fluoride. No indication was found of any compound that might contain boron trifluoride.

Previous work [5] established that Teflon burns in 15 to 20 atm. of fluorine with carbon tetrafluoride as the only major product. Higher fluorocarbons are not detected in the products of combustion in amounts greater than 0.1 percent. The method of analyses was the absorption in mercury of the fluorine from a sample of bomb gases resulting from combustion of Teflon and the analysis of the residual gases by a mass spectrometer.

The same test revealed $CF_4$ among the combustion products of the aluminum boride-Teflon mixtures. However, this test did not reveal the boron trifluoride suspected among the products. Under the conditions of the reaction of fluorine with mercury, we suspected interaction between boron trifluoride and the mercury fluoride with the formation of a solid mercury fluoborate such as $Hg(BF_4)_2$ or $Hg_2(BF_4)_2$. The condensed phase residue from the fluorine absorption was treated with acid to dissolve the soluble mercury compound. The solution was treated with calcium ion and with nitron reagent, but did not give a positive test for fluoborate ion.

The possibility of absorbing $BF_3$ from its mixture with fluorine by passage over a heated non-volatile metal fluoride was considered, but no procedure was worked out.

Boron trifluoride was identified among the combustion products by infrared spectroscopy. A sample of bomb gases was examined in the region from 650 to 400 $cm^{-1}$, and the $BF_3$ band at 481 $cm^{-1}$ was observed. Also present in the spectrum was the $CF_4$ band at 630 $cm^{-1}$. Spectra of the evacuated cell and of $BF_3$ alone were taken in the region mentioned above to substantiate the identification. The cell used was 8 cm long and had polyethylene windows, 0.0625 in. thick.

Some unburned carbon was observed in the combustion experiments involving Teflon alone. The amount was estimated to be 0.2 to 0.8 mg. It was not definitely known that a carbon residue was also obtained in the combustion of the aluminum boride-Teflon mixtures, but a residue was assumed to have been present. The possible presence of carbon was obscured by small amounts of dark material resulting from incomplete combustion of the aluminum borides. This dark material was more prominent in the combustion of $AlB_2$ than in the combustion of $\alpha$-$AlB_{12}$.

## 5.7 Calibration Experiments

Six calibration experiments were made in which benzoic acid (Standard Sample 39i) was burned in 30 atm of oxygen in the nickel combustion bomb. In addition to the fittings of the standard bomb used in the fluorine combustion experiments, the bomb contained one ml of water and a platinum crucible. The aluminum electrodes were removed. Instead of a tungsten wire the fuse consisted of two cm of platinum wire of 0.004 in. diam. The mass of benzoic acid used (1.70 g) was sufficient to cause a three-degree temperature rise. The nitric acid titration usually made at the conclusion of a combustion experiment using oxygen was so small that it could be neglected because high purity oxygen was used. The energy equivalent of the standard calorimeter, containing 16 atm fluorine and corrected for removal of the other non-standard features mentioned above, was found to be 146,905.5 ±7.0 j $ohm^{-1}$. The change of the bomb from the oxygen experiments to the fluorine experiments required an adjustment of 13.2 j $ohm^{-1}$ in the energy equivalent. The uncertainty given is the standard deviation of the mean.

## 5.8 Fluorine Combustion Experiments

Seven heat measurements were made on the combustion of Teflon in fluorine, five on $AlB_2$-Teflon mixtures and nine on $\alpha$-$AlB_{12}$-Teflon mixtures. About 16.5 atm. fluorine was used in all of the experiments with the borides and two of the experiments with Teflon alone. For the other experiments with Teflon a pressure of about 21.4 atm. fluorine was used. In each experiment, the sample pellet was placed in the recess of the pellet holder, and the bomb was filled with fluorine.

After a combustion experiment and disposal of the excess fluorine, the solid aluminum fluoride product was collected for later analysis. All bomb parts (bomb base, bomb head assembly and electrodes, liner, and pellet holder) were weighed before the first experiment and after each of the experiments. The bomb parts were washed with water and dried before the weighings were made.

Tables 5.80, 5.81 and 5.82 give the data for individual experiments on Teflon, aluminum diboride, and α-aluminum dodecaboride, respectively. The numbered entries are as follows:

(1) Masses of the constituents of a pellet introduced into the bomb prior to combustion, corrected for weight loss in preparation of the pellet.

(2) Pressure of fluorine introduced into the bomb prior to combustion.

(3) Energy equivalent of the calorimeter for a given experiment.

(4) Resistance change of the calorimeter thermometer, corrected for heat of stirring and heat transfer.

(5) Total energy change in the bomb process.

(6) Energy liberated by the tungsten fuse wire, assuming the fuse burns according to the reaction:

$$W(s) + 3F_2(g) = WF_6(g)$$

From the heat of formation of $WF_6$ [10] we calculate 9.440 j $mg^{-1}$ for the energy of combustion of the fuse.

(7) Correction of the bomb reaction from actual conditions to standard states at 298°K. These corrections comprise the following: (a) the net correction for compression and decompression of the bomb gases to standard states, (b) the correction for conversion of $\Delta E_T^\circ$ to $\Delta H_T^\circ$ at the temperature of the bomb process, and (c) the correction $\Delta H^\circ_{298^\circ} - \Delta H_T^\circ$ for the actual bomb reaction.

(8) Standard state enthalpy change due to combustion of the Teflon used as a binder ($\Delta H_c^\circ$ = 10,378.2 j $g^{-1}$).

(9) Standard state enthalpy change due to combustion of the aluminum boride sample (including impurities).

(10) Standard state enthalpy change due to combustion of impurities in the aluminum boride.

(11) Standard state enthalpy change due to combustion of aluminum boride.

(12) Mass of aluminum boride, corrected for impurities and recovery of unburnt boride.

(13) Standard enthalpy of combustion, $\Delta H^{\circ}_{298}$ of the subject compound of the table.

(14) Average value of the standard enthalpy of combustion of the subject compound of the table.

(15) Uncertainty (standard deviation of the mean) of the average heat of combustion.

The heat capacities at constant pressure, Cp, used in the calculation of entry (6) (Tables 5.80, 5.81, 5.82) are as follows in cal $deg^{-1}$ $gram^{-1}$ at 25°C: aluminum, 0.216 [11]; boron, 0.245 [12]; Teflon, 0.28 [13]; aluminum fluoride, 0.213 [11]; fluorine, 0.197 [14]; carbon tetrafluoride, 0.166 [15]; boron trifluoride, 0.1778 [12]; aluminum diboride , 0.0907 and α-aluminum dodecaboride, 0.0853. The heat capacities of $AlB_2$ and α-$AlB_{12}$ were estimated by assuming the molar heat capacities of the compounds to be the sums of the atomic heat capacities of the elements. The heat capacity at constant volume, Cv, used for fluorine was 5.50 cal $deg^{-1}$ $mole^{-1}$ [14]. The coefficients $\left[\frac{\partial E}{\partial P}\right]_T$ required to convert $\Delta E$ to $\Delta E^{\circ}$ were estimated by the method of Hirschfelder, Curtiss and Bird [16] from the force constants for $F_2$ [17], $CF_4$ [18] and $BF_3$ [19].

In calculating the corrections for the combustion of impurities and in calculating the heats of formation of the aluminum borides, the following values, in kcal $mole^{-1}$, were used for the heats of formation of other compounds: $AlF_3$, -360.4 [5]; $BF_3$ -269.88 [25]; $CF_4$, -220.4 [26]; $Al_2O_3$, -400.29 [20]; $B_2O_3$, -305.34 [8], $Al_4C_3$, -43.0 [21]; $B_4C$, -12.2 [12,22]; AlN, -76.1 [23]; BN, -59.51 [24]; $MgF_2$, -265.02 [27]; $CaF_2$, -290.3 [28]; $SiF_4$, - 385.98 [29]; $FeF_3$, -243.1 [28]; $CuF_2$, -126.9 [28]; $MnF_3$ -238 [30].

Atomic weights were taken from the 1961 table of atomic weights based on carbon -12 adopted by the International Union of Pure and Applied Chemistry [9]. The unit of energy is the joule, and the calorie was taken as 4.1840 joules.

TABLE 5.80

TEFLON COMBUSTION EXPERIMENTS

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| (1) | Mass Teflon, grams | 4.229495 | 4.319060 | 4.286609 | 4.285883 | 4.358344 | 4.354427 | 4.362010 |
| (2) | $F_2$ Pressure, Atm. | 21.4 | 21.5 | 21.5 | 16.5 | 16.4 | 21.4 | 20.8 |
| (3) | En. Eq. j $ohm^{-1}$ | 146,974.1 | 146,975.4 | 146,975.1 | 146,957.8 | 146,914.2 | 146,931.4 | 146,929.6 |
| (4) | $\Delta R_c$ ohms | 0.298949 | 0.305201 | 0.302915 | 0.302723 | 0.307970 | 0.307782 | 0.308312 |
| (5) | (En. Eq.) ($\Delta R_c$) j | -43,937.9 | -44,857.0 | -44,521.0 | -44,489.4 | -45,245.2 | -45,222.8 | -45,300.2 |
| (6) | Fuse Corr., j | 36.9 | 37.6 | 32.3 | 35.1 | 14.9 | 13.7 | 15.5 |
| (7) | Std. State Corr. j | 0.9 | -0.7 | -0.1 | 5.6 | 6.2 | -0.4 | 0.4 |
| (13) | $\Delta H^{\circ}_{298}$ Comb., j $gram^{-1}$ | -10,379.9 | -10,377.3 | -10,378.6 | -10,371.0 | -10,376.4 | -10,382.4 | -10,381.5 |
| (14) | Average $\Delta H^{\circ}_{298}$ Comb. | -10,378.2 joules $gram^{-1}$ | | | | | | |
| (15) | Std. Dev. of Mean | ±1.4 joules $gram^{-1}$ | | | | | | |

TABLE 5.81

ALUMINUM DIBORIDE COMBUSTION EXPERIMENTS

| | | | | | | |
|---|---|---|---|---|---|---|
| (1) | Mass Teflon, grams | 1.867789 | 2.002876 | 1.931070 | 2.026707 | 2.035980 |
| | Mass $AlB_2$, grams | 0.347130 | 0.315427 | 0.289270 | 0.302112 | 0.289617 |
| (2) | $F_2$ Pressure, atm. | 16.4 | 16.5 | 16.4 | 16.5 | 16.6 |
| (3) | En. Eq., j $ohm^{-1}$ | 146,931.0 | 146,932.6 | 146,931.3 | 146,932.8 | 146,933.2 |
| (4) | $\Delta R_c$, ohms | 0.306261 | 0.300104 | 0.282498 | 0.294872 | 0.289731 |
| (5) | (En. Eq.) $(\Delta R_c)$, j | -44,999.2 | -44,095.1 | -41,507.8 | -43,326.4 | -42,571.1 |
| (6) | Fuse Corr., j | 41.6 | 42.3 | 41.7 | 42.3 | 41.5 |
| (7) | Std. State Corr., j | -52.6 | -47.9 | -44.1 | -45.9 | -44.2 |
| (8) | $-\Delta H^\circ$, Teflon | 19,384.3 | 20,786.2 | 20,041.0 | 21,033.6 | 21,129.8 |
| (9) | $\Delta H^\circ$, $AlB_2$ | -25,625.9 | -23,314.5 | -21,469.2 | -22,296.4 | -21,444.0 |
| (10) | $\Delta H^\circ$, impurities, j | 253.2 | 230.2 | 211.1 | 220.6 | 211.4 |
| (11) | $\Delta H^\circ$, $AlB_2$ Corr., j | -25,372.7 | -23,084.3 | -21,258.1 | -22,075.8 | -21,232.6 |
| (12) | Mass $AlB_2$, Corr. grams | 0.337280 | 0.306526 | 0.281092 | 0.293646 | 0.281452 |
| (13) | $\Delta H^\circ$, Comb. j $gram^{-1}$ | -75,227.4 | -75,309.4 | -75,626.8 | -75,178.3 | -75,439.5 |
| (14) | Ave. $\Delta H^\circ$ Comb. j $gram^{-1}$ | -75,356.3 joules $gram^{-1}$ | | - 917.24 kcal $mole^{-1}$ | | |
| (15) | Std. Dev. of Mean | ±80.8 joules $gram^{-1}$ | | ±0.98 kcal $mole^{-1}$ | | |

TABLE 5.82

α-ALUMINUM DODECABORIDE COMBUSTION EXPERIMENTS

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (1) Mass Teflon, g | 1.763350 | 1.760174 | 1.754560 | 1.763418 | 1.770681 | 1.771629 | 1.770132 | 1.784725 | 1.781965 |
| Mass α-$AlB_{12}$, g | 0.312340 | 0.319124 | 0.306422 | 0.311375 | 0.286025 | 0.304906 | 0.305405 | 0.345418 | 0.318867 |
| (2) $F_2$ Pressure, atm. | 16.3 | 16.2 | 16.4 | 16.5 | 16.6 | 16.6 | 16.6 | 16.4 | 16.6 |
| (3) En. Eq., j $ohm^{-1}$ | 146,929.2 | 146,929.2 | 146,930.0 | 146,929.8 | 146,929.0 | 146,929.6 | 146,929.6 | 146,929.6 | 146,929.7 |
| (4) $\Delta R_c$, ohms | 0.322584 | 0.327284 | 0.318447 | 0.321869 | 0.306640 | 0.318749 | 0.318731 | 0.344888 | 0.327758 |
| (5) (En.Eq.)($\Delta R_c$), j | -47,397.0 | -48,087.6 | -46,789.4 | -47,292.1 | -45,054.3 | -46,833.7 | -46,831.0 | -50,674.3 | -48,157.4 |
| (6) Fuse Corr., j | 41.7 | 37.4 | 37.5 | 36.9 | 36.2 | 31.8 | 42.1 | 42.0 | 42.5 |
| (7) Std. State Corr., j | -45.5 | -46.3 | -44.7 | -45.5 | -42.1 | -44.7 | -44.7 | -49.7 | -46.6 |
| (8) $-\Delta H^\circ$, Teflon, j | 18,300.4 | 18,267.4 | 18,209.2 | 18,301.6 | 18,376.5 | 18,386.3 | 18,370.8 | 18,522.2 | 18,493.6 |
| (9) $\Delta H^\circ$, α-$AlB_{12}$, g | -29,100.4 | -29,829.1 | -28,587.4 | -28,999.1 | -26,683.7 | -28,460.3 | -28,462.8 | -32,159.8 | -29,667.9 |
| (10) $\Delta H^\circ$, Impurities, j | 256.5 | 262.2 | 252.0 | 255.8 | 234.9 | 250.4 | 250.9 | 283.7 | 261.9 |
| (11) $\Delta H^\circ$, α-$AlB_{12}$ Corr. j | -28,843.9 | -29,566.9 | -28,335.4 | -28,743.3 | -26,448.8 | -28,209.9 | -28,211.9 | -31,876.1 | -29,406.0 |
| (12) Mass α-$AlB_{12}$ Corr. g | 0.304022 | 0.310623 | 0.298248 | 0.303049 | 0.278393 | 0.296769 | 0.297240 | 0.336203 | 0.310358 |
| (13) $\Delta H^\circ$, Comb. j $g^{-1}$ | -94,874.4 | -95,185.8 | -95,006.2 | -94,847.0 | -95,005.3 | -95,056.8 | -94,912.9 | -94,812.1 | -94,748.6 |
| (14) Ave. $\Delta H^\circ$ Comb. j $g^{-1}$ | -94,938.8 joules $gram^{-1}$ | | | | -3546.2 kcal $mole^{-1}$ | | | | |
| (15) Std. Dev. of Mean | ±45.6 joules $gram^{-1}$ | | | | ±1.7 kcal $mole^{-1}$ | | | | |

## 5.9 Discussion and Results

No correction was applied to any experiment for the small amount of unburned carborn resulting from the combustions of the Teflon. It was assumed that the carbon formation took place in all experiments approximately in proportion to the amount of Teflon present. The heat of combustion per gram of Teflon would therefore be constant and the error due to carbon formation would be eliminated when the energy due to combustion of Teflon was subtracted from the total energy released in the combustion.

A slow premature reaction was detected prior to ignition of the aluminum diboride samples. The rate of temperature rise during the fore-period, when the calorimeter is about three degrees below the jacket temperature, was observed to be $4 \times 10^{-5}$ to $5 \times 10^{-5}$ ohm $min^{-1}$ higher than normal and led to unusually high apparent values for the calorimeter "cooling constant". Upon reweighing an $AlB_2$-Teflon pellet after exposure to fluorine, a significant increase in weight was observed.

In the heat measurements in which $\alpha$-$AlB_{12}$-Teflon pellets were burned, values of the calorimeter "cooling constant" were normal and no significant weight gain was observed in a pellet after exposure to fluorine.

An estimate of the unmeasured heat due to the premature reaction of $AlB_2$ was made from a straight line fitted by least squares to the heat of combustion plotted as a function of the apparent "cooling constant". The data and derived equation are shown in Table 5.90. By extrapolation to the normal drift rate of the calorimeter, a heat of combustion more negative by 6.3 kcal $mole^{-1}$ than the average of the uncorrected heats of combustion was obtained. An uncertainty of 1.7 kcal $mole^{-1}$ (which is two times the standard error of estimate) is assigned to this value, to allow for uncertainties in the linear equation and for normal fluctuations in the fore-period drift rate.

TABLE 5.90

ESTIMATE OF FORE-PERIOD REACTION OF ALUMINUM DIBORIDE

| Ordinate $\Delta H_c^\circ$, kcal $mole^{-1}$ | Abscissa k, cooling constant |
|---|---|
| 915.67 | 222.2 |
| 916.67 | 216.4 |
| 920.53 | 211.4 |
| 915.07 | 225.0 |
| 918.25 | 214.7 |

$\Delta H_c^\circ = -0.373156k + 998.186$

Under normal operation, the "cooling constant", k, is equal to 200.0. Using the above equation, $\Delta H_c^\circ$ was found equal to 923.5 kcal mole$^{-1}$ when k equals 200.0. The correction applied to the determined heat of combustion of $AlB_2$ for the fore-period reaction was 6.3 kcal mole$^{-1}$.

Incomplete combustion occurred in both the aluminum diboride and α-aluminum dodecaboride experiments. The degree of completeness was greater in the experiments with α-$AlB_{12}$, and it was in some cases impossible to see any unburnt boride remaining. In the experiments with $AlB_2$ some unburnt boride was always present. An analysis for unreacted $AlB_2$ and α-$AlB_{12}$ was performed by the NBS Applied Analytical Research Section using a procedure developed by Ross, Meyer, and White [31] for determining boron in fluoride salts. The method consisted of fusion of the aluminum fluoride - aluminum boride residues followed by solution in acid and extraction with an organic solvent. The boron in the organic phase was determined spectrophotometrically with carminic acid. The recovery of $AlB_2$ ranged between 0.10 to 0.24 mg. while that for α-$AlB_{12}$ was between 0.01 and 0.04 mg.

## 5.10 Treatment of Impurities

Because of the complicated compositions of the aluminum boride samples, it was not possible to calculate the heats of formation of aluminum diboride and α-aluminum dodecaboride unabmiguously from the measured heats of combustion, which are shown as entry (14) in Tables 5.81 and 5.82, respectively. Two factors which present difficulties in both compounds are (a) the non-stoichiometric ratio of boron to aluminum, and (b) the presence of non-metallic elements principally nitrogen, oxygen and carbon, which are presumably combined with aluminum and boron, but in unknown proportions. The presence of several minor metallic impurities does not contribute an appreciable uncertainty in comparison to the non-metals.

When one considers the possible distribution of the non-metallic impurities in compounds of aluminum and boron, two fairly clearly defined possibilities present themselves. First the compound of aluminum and boron can be considered to be stoichiometric, and the non-metals can be assumed to be combined entirely with one element. Any excess of aluminum or boron remaining is assumed to be present as the free element. This situation gives two extreme possibilities, depending upon which element is presumed to be combined with the non-metals. Both aluminum diboride and α-aluminum dodecaboride have been treated in this way and the two extreme analyses are shown in Tables 5.100 and 5.101 as columns (1) and (2). In treatment (1) the non-metals are combined entirely with aluminum, and in treatment (2) they are combined entirely with boron. Secondly, the compound of aluminum and boron can be considered to be non-stoichiometric, and the non-metallic impurities distributed between boron and aluminum in proportion to the relative numbers of moles of boron and aluminum. In this situation the measured atomic ratios lead to non-stiochiometric compounds having the formulas $AlB_{2.215}$ and α-$AlB_{11.96}$. These formulas

were adopted for calculation of the results which are considered to be most probably correct. The sample compositions on this basis are shown in Tables 5.100 and 5.101 as column (3). This latter treatment is considered to be the most probable than can be devised in the absence of specific information about the distribution of the elements. We believe the most probable atomic configuration in the case of $AlB_2$ is a lattice in which some aluminum atom sites are either vacant or have been filled with boron atoms. The deviation of the $\alpha$-$AlB_{12}$ from stoichiometry was not significant, but the observed ratio was used for consistency.

TABLE 5.100

COMPOSITION OF ALUMINUM DIBORIDE (% BY WEIGHT)

| Constituent | (1) | (2) | (3) |
|---|---|---|---|
| $AlB_2$ | 90.532 | 93.976 | --- |
| $AlB_{2.215}$ | --- | --- | 97.232 |
| B | 6.027 | 3.541 | --- |
| $Al_2O_3$ | 2.091 | --- | 0.651 |
| $B_2O_3$ | --- | 1.427 | 0.983 |
| AlN | 0.865 | --- | 0.269 |
| BN | --- | 0.524 | 0.360 |
| $Al_4C_3$ | 0.315 | --- | 0.181 |
| $B_4C$ | --- | 0.362 | 0.154 |
| Fe | 0.025 | 0.025 | 0.025 |
| Cu | 0.075 | 0.075 | 0.075 |
| Si | 0.026 | 0.026 | 0.026 |
| Mg | 0.024 | 0.024 | 0.024 |
| Ca | 0.013 | 0.013 | 0.013 |
| Mn | 0.01 | 0.01 | 0.01 |
| Total | 100.003 | 100.003 | 100.003 |

TABLE 5.101

COMPOSITION OF α-ALUMINUM DODECABORIDE (% BY WEIGHT)

| Constituent | (1) | (2) | (3) |
|---|---|---|---|
| $AlB_{12}$ | 88.273 | 97.130 | --- |
| $AlB_{11.96}$ | --- | --- | 97.340 |
| Al | --- | 0.264 | --- |
| B | 8.313 | --- | --- |
| $Al_2O_3$ | 2.758 | --- | 0.213 |
| $B_2O_3$ | --- | 1.883 | 1.738 |
| $Al_4C_3$ | 0.438 | --- | 0.088 |
| $B_4C$ | --- | 0.505 | 0.404 |
| Mg | 0.150 | 0.150 | 0.150 |
| Si | 0.050 | 0.050 | 0.050 |
| Ca | 0.018 | 0.018 | 0.018 |
| Total | 100.000 | 100.000 | 100.001 |

## 5.11 Heats of Formation of the Aluminum Borides

The heat of combustion of $AlB_{2.215}$ listed in Table 5.81 is for one mole of reaction (1):

$$AlB_{2.215}(s) + \frac{9.645}{2} F_2(g) \rightarrow AlF_3(s) + 2.215\ BF_3(g) \qquad (1)$$

From the heat measurements and the auxiliary data listed above, we calculate the heat of formation of $AlB_{2.215}$ to be $-34.7 \pm 2.1$ kcal mole$^{-1}$. The calculation of this quantity and of the uncertainty (standard deviation of the mean) is summarized in Table 5.110.

TABLE 5.110

COMBUSTION DATA ON ALUMINUM DIBORIDE

| Description of Data | Heat Data kcal mole$^{-1}$ | Uncertainty (Std. Dev. of Mean) kcal mole$^{-1}$ |
|---|---|---|
| Obs. Heat of Combustion, $\Delta H^\circ_{298}$ | -917.2 | ±0.98 |
| Corr. for fore-period reaction | - 6.3 | ±1.7 |
| Corr. Heat of Combustion, $\Delta H^\circ_{298}$ | -923.5 | ±2.0 |
| $\Sigma \Delta H^\circ_{f298}$ for products | -958.2 | ±0.67 |
| $\Delta H^\circ_{f298}$ [$AlB_{2.215}$] | - 34.7 | ±2.1 |

The heat of combustion of $\alpha$-$AlB_{11.96}$ listed in Table 5.82 is for one mole of reaction (2).

$$\alpha\text{-}AlB_{11.96}(s) + \frac{38.88}{2} F_2(g) \rightarrow AlF_3(s) + 11.96\ BF_3(g) \qquad (2)$$

From the heat measurement and auxiliary data listed above, we calculate the heat of formation of $\alpha$-$AlB_{11.96}$ to be $-42.0 \pm 1.8$ kcal mole$^{-1}$. The calculation of this quantity and of the uncertainty (standard deviation of the mean) is summarized in Table 5.111.

TABLE 5.111

COMBUSTION DATA ON $\alpha$-ALUMINUM DODECABORIDE

| Description of Data | Heat Data kcal mole$^{-1}$ | Uncertainty (Std. Dev. of Mean) kcal mole$^{-1}$ |
|---|---|---|
| Obs. Heat of Combustion, $\Delta H^{\circ}_{298^{\circ}}$ | -3546.2 | ±1.7 |
| $\Sigma\Delta H^{\circ}_{f298^{\circ}}$ for products | -3588.2 | ±0.47 |
| $\Delta H^{\circ}_{f298^{\circ}}$ [$\alpha$-$AlB_{11.96}$] | - 42.0 | ±1.8 |

Because of the relatively large amounts of impurities in the samples, we have attempted to estimate limits to the uncertainties introduced into the calculated heats of formation of the borides by the lack of knowledge of the exact nature of the impurities. This has been done by using the compositions of the samples listed in Tables 5.100 and 5.101 as columns (1) and (2), respectively. The heats of formation of aluminum diboride and $\alpha$-aluminum dodecaboride, calculated by assuming these distributions of non-metallic impurities between aluminum and boron, are shown in Table 5.112. The values listed for treatments (1) and (2) differ from those obtained by treatment (3) in that they refer to the stoichiometric rather than to the non-stoichiometric compounds. Inspection of Table 5.112 shows that the heats of formation calculated using treatment (3) are extremely close to the heats of formation calculated using treatments (1) and (2), and do not differ more than 0.4 kcal mole$^{-1}$ from either of them. It is evident that an indefinite number of distributions other than the ones selected are possible. Because of the manner of assigning the compositions used in treatments (1) and (2), we feel that the heats of formation derived by using them represent approximate extremes to the values that would be obtained using any accessible composition.

TABLE 5.112

DEPENDENCE OF DERIVED HEATS OF FORMATION ($\Delta H^{\circ}_{f298}$, kcal mole$^{-1}$) OF ALUMINUM BORIDES UPON THE METHOD OF TREATMENT OF IMPURITIES

| Assumed Sample Composition (See Tables 5.100 and 5.101) | (1) | (2) | (3) |
|---|---|---|---|
| Formula | | | |
| $AlB_2$ | -34.8 | -34.5 | |
| $AlB_{2.215}$ | | | -34.7 |
| $\alpha$-$AlB_{12}$ | -42.1 | -42.4 | |
| $\alpha$-$AlB_{11.96}$ | | | 42.0 |

For correlation of the heats of formation of borides it is more informative to use the heat of formation per gram atom of boron. The heat of formation of $AlB_{2.215}$ is -15.7 kcal/(gram-atom of boron). The heat of formation of $\alpha$-$AlB_{11.96}$ is -3.51 kcal/(gram-atom of boron).

For thermodynamic studies on the binding energies of intermetallic compounds such as these, we suggest that the most useful parameter should be the heat of formation per gram-atom of both metals together. Using this parameter, the heat of formation of $AlB_{2.215}$ is -10.8 kcal/gram-atom and that of $\alpha$-$AlB_{11.96}$ is -3.24 kcal/gram-atom.

## 5.12 Conclusions

1. The heats of combustion of $AlB_{2.215}$ and $\alpha$-$AlB_{11.96}$ were determined using fluorine bomb calorimetry and were found to be -34.7 and -42.0 kcal mole$^{-1}$ respectively.

2. The accuracies of the heats of combustion of both are limited by corrections necessary for the combustion of impurities, and for incomplete combustion. An additional limitation on the accuracy of the heat of combustion of $AlB_2$ is caused by a premature reaction that could not be accurately measured. The accuracies of the heats of formation of the compounds are limited by the uncertainties in the heats of combustion, and by the small uncertainty in the actual proportions of aluminum and boron present. Because the heat of formation is a relatively small number determined by difference from two large numbers, there is a relatively large fractional uncertainty in it.

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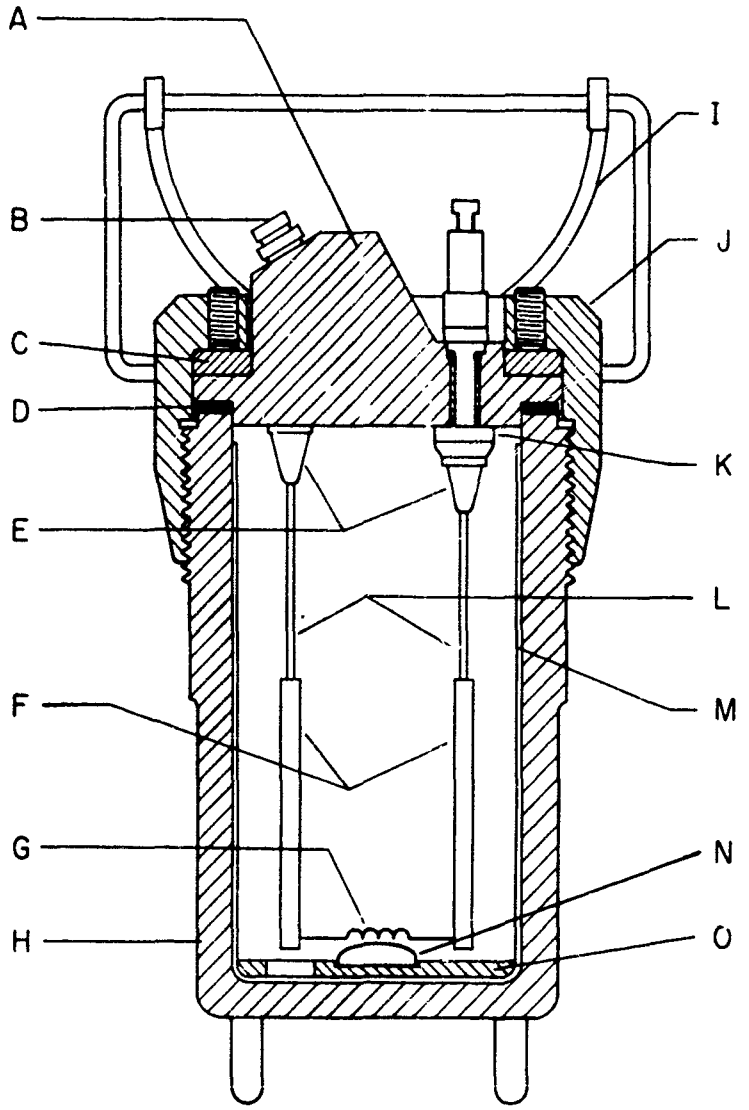


FIG. I FLUORINE COMBUSTION BOMB

A. NICKEL BOMB HEAD
B. NEEDLE VALVE
C. MONEL PRESSURE PLATE
D. TEFLON GASKET
E. MONEL LOCK NUT
F. ALUMINUM ELECTRODE
G. FUSE
H. BOMB BODY
I. HANDLE
J. SCREW CAP
K. ALUMINA WASHER
L. MONEL ROD
M. TYPE 304 STAINLESS STEEL LINER
N. PELLET
O. PELLET HOLDER

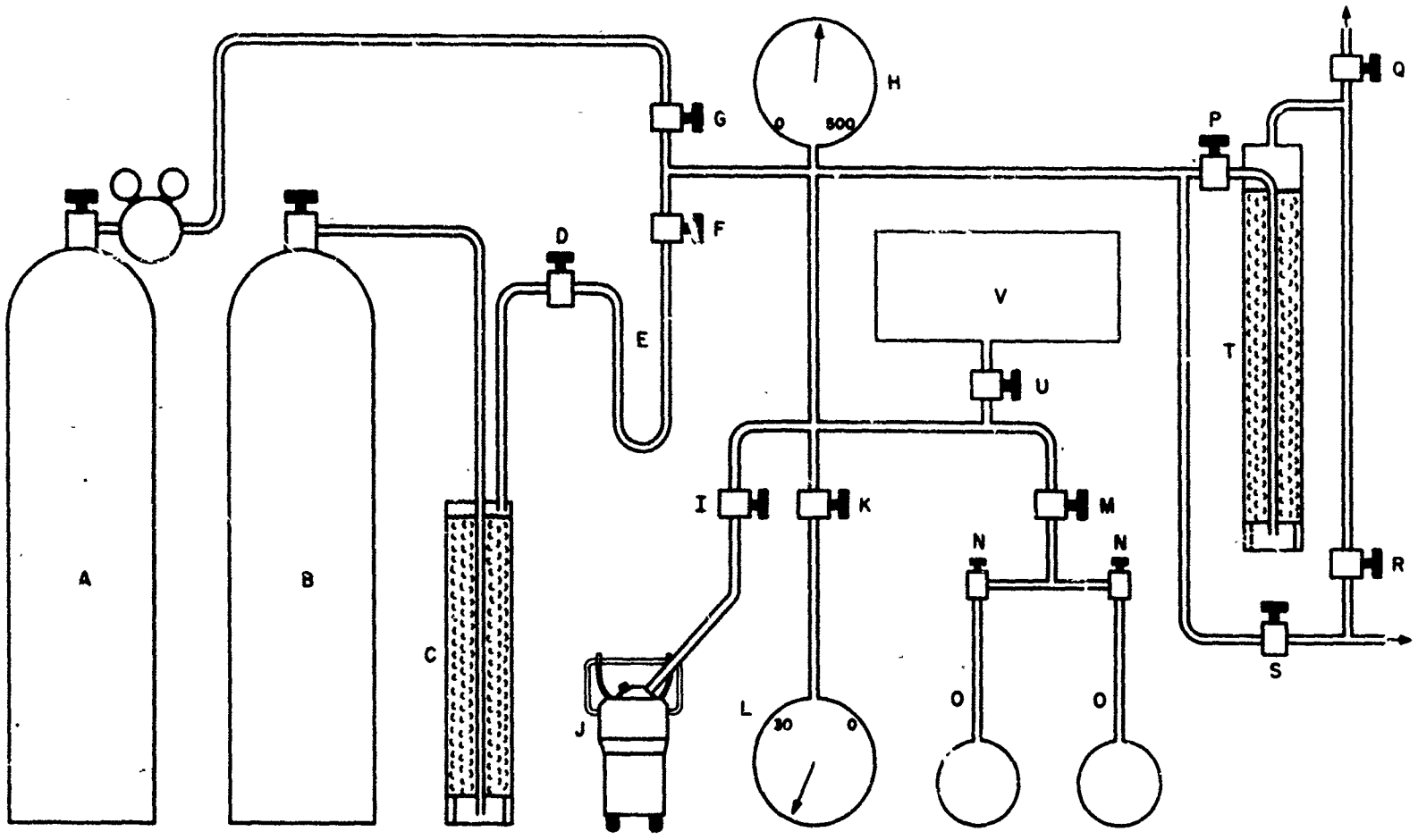


FIG. 2 SCHEMATIC DIAGRAM OF FLUORINE MANIFOLD

A. HELIUM
B. FLUORINE
C. HYDROGEN FLUORIDE TRAP
D. FLUORINE VALVE
E. LIQUID NITROGEN TRAP FOR FLUORINE
F. FLUORINE VALVE TO MANIFOLD
G. HELIUM VALVE TO MANIFOLD
H. PRESSURE GAUGE (0-500 P.S.I.)
I. VALVE TO BOMB
J. BOMB
K. VALVE TO VACUUM GAUGE
L. VACUUM GAUGE (0-30 IN. Hg)
M,N. VALVES TO GAS-SAMPLE COLLECTOR BULBS
O. GAS-SAMPLE COLLECTOR BULBS
P. VALVE TO FLUORINE ABSORPTION TOWER
Q. VENT VALVE TO FUME HOOD
R. VALVE TO VACUUM VIA FLUORINE ABSORPTION TOWER
S. VALVE DIRECT TO VACUUM
T. FLUORINE ABSORPTION TOWER
U. VALVE TO BALLAST TANK
V. BALLAST TANK

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